



Alteration of volatile compounds profile of brewers' spent grain by bath-ultrasonication and its combination with conventional water-bath and autoclave treatment

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ABSTRACT

The study aimed to investigate the capability of bath-ultrasonication and its combination with conventional water-bath and autoclave treatment in modifying the volatile composition of brewers' spent grain (BSG). It was hypothesized that the treatments modified the volatile composition of BSG due to the sonochemical modification. The results demonstrated that the treatments intensified the desirable odor and removed the undesirable one which might allow the possibility of masking and renewing the odor perception of BSG. Besides the influence on odor perception related compounds, it is worth to highlight that the treatments eliminated herbicidal compounds such as (E,E)-2,4-heptadienal and (E)-2-hexenal which might be present from herbicidal treatment. Combination of bath-ultrasonication with autoclave treatment modified the volatile aldehydes while its combination with conventional water-bath generated the same profile as it was in untreated BSG. Time elevation on bath-ultrasonication had no significant impact on the amount of ketones and alkanes, while the fluctuation occurred as an impact of thermal exposures. Moreover, the treatment reduced the amount of alcohol and increased the fatty acids. In conclusion, bath-ultrasonication and its combination with thermal exposure modified the volatile compositions of BSG.

1. Introduction

Ultrasonication has been increasingly evaluated for improving nutritional value of food and agro-based products. Ultrasonication is known for its benefits as less solvent utilization and environmental friendly [1]. It improved the recovery of the extraction of cellulose from spent coffee [2], protein from rice bran [3] and lycopene from tomato peels [4]. Ultrasonication (bath type) has been reported to intensify the amount of reducing sugar and protein, reduce the protein aggregation, and decrease the amount of bound and free phenolics in brewers' spent grain (BSG) [5,6]. However, the modification of volatile composition on BSG due to the sonoprocessing has never been investigated. BSG is a complex material in which the chemical constituents are bound and/or entrapped including volatile compounds. Seeing the high possibility of BSG to be incorporated in food products, the alteration of its volatile compositions is seemingly important to be evaluated.

BSG is a byproduct of brewery industry, which has been evaluated for its potential as a healthy food ingredient [7]. BSG is composed of dietary fiber, protein, fat, phenolic acids and minerals [8–10] thus possessing certain biological activities. BSG extracts acted as a DNA-protective and antimutagenic [11], antithrombotic and blood anticoagulant [10] as well as maintaining colon health [12]. These mentioned biological properties had been aligned with the improvement in the nutritional value of BSG-added food products [7]. BSG has been applied into food products including dough and bread making, extruded products, cookies, baked snack, biscuits, and pasta [13]. The behavior and impacts of BSG in food processing and final products has been studied previously [13]. On one hand, BSG enhanced the nutritional value of BSG-added products and on the other hand, BSG issued sensory perception in addition to the mechanical processing efficiency and textural properties [13].

Several outstanding studies have highlighted the benefits of

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ultrasound on food processing [1,14–17]. Valorisation of agro-based industrial organic waste, particularly its protein, phenolic and other nutritional-related compounds extraction, can be optimized by ultrasound treatments [1]. However, the study on the influence of ultrasound in odor (volatile) compounds is very limited to this day. As an impact of sonolysis, ultrasound has been reported to develop pleasant flavor compounds in plain chocolate and unpleasant taste in milk [15]. As highlighted, assessment in consumer acceptability of ultrasound-treated food ingredients is highly needed [18]. Volatile composition is one of the important factors in terms of food product acceptability. Therefore, the specific impact of ultrasound in technological and functional properties of food products must be strongly taken into consideration. Ultrasonication can act synergistically with temperature and pressure to achieve higher benefits [19]. Therefore, the study aimed to investigate the ability of sound waves (bath-ultrasonication) and its combination with thermal treatments (autoclave and conventional water-bath) to modify the profile of volatile compounds on BSG. It was hypothesized that bath-ultrasonication and its combination with autoclave treatment and conventional water-bath might eliminate some of the volatile compounds and at the same time form certain compounds, particularly aldehydes, ketones, alcohol, alkanes, fatty acids, furan and other compounds.

2. Materials and methods

2.1. Materials

BSG was obtained from a local light-beer producer in Wrocław, Poland. After that, BSG was ground to pass 0.2 mm, stored at $-20\text{ }^{\circ}\text{C}$ in a polyethylene bag prior to the experiment.

2.2. Experimental design

Firstly, BSG was allowed to unfreeze, mixed properly in a beaker glass with distilled water (1:1) and closed with aluminum foil. The mixture was treated with bath-ultrasonication (Fisher Scientific, Elmasonic S30 H, Germany) with ultrasonic frequency 37 KHz, power 80 W, 115–120 V/220–240 V. According to a previous study [1], intensity, time exposure and combined methods influenced the results of ultrasonication treatment. Acoustic cavitation is more efficient at low temperatures [14]; therefore, the study was controlled at room temperature. While a higher solubility might be obtained as the solution temperature increases [14] and the synergistic effect of ultrasound combined with thermal treatments has been extensively emphasized [19]. Therefore, the study combined ultrasound followed by thermal exposures (conventional water-bath and autoclave treatment). Our preliminary study revealed that conventional water-bath has been able to modify the chemical composition, antioxidant activity and functionality of BSG (unpublished data) and autoclave treatment was able to convert the insoluble dietary fiber into soluble one, thus improving the antioxidant activity as well as intensifying the polyphenolic compounds of BSG [20–22]. The study was conducted on 3 different time exposures including 5, 15 and 25 min at room temperature. Time exposures were chosen in consideration of undergoing treatments to thermal exposures. Although 60 min exposure with lower power has been identified as an optimal condition for BSG treatment [5], current study combined with thermal treatments. Therefore, reducing time exposures on ultrasound treatment is appropriate. Furthermore, rice bran and spent coffee, high polysaccharide materials, were exposed to ultrasound upto 40 min [2,3]. Combination of ultrasound with thermal exposures was then designed at a lower level. The sonicated mixture was then combined with 2 different thermal treatments including conventional water-bath heating at $90\text{ }^{\circ}\text{C}$ for 30 min and autoclave heating at $110\text{ }^{\circ}\text{C}$ for 12 min, as a medium exposure according to a preliminary study. The control was provided by ultrasound treatment with no thermal exposure applied. Therefore, 9 samples were obtained. All the treatments were done in duplicate and

the assessment of volatile compounds was done in at least duplicate. The treated BSG was then dried in an oven dryer at $75\text{ }^{\circ}\text{C}$ overnight to reach the moisture content below 6 %. After that, BSG was ground and passed through a lab-scale sieving machine to obtain particle size $\leq 0.2\text{ mm}$ and stored at $10\text{ }^{\circ}\text{C}$ for further analysis.

2.3. Analysis of volatile compounds

The analysis of volatile compounds was done according to the procedures described in previous studies [23,24] with some modification. Previous study used sodium chloride solution to the BSG [23] while the current study used distilled water. The sample was mixed with distilled water at a ratio of 1:2 and closed properly. The isolation of volatile compounds was done by headspace solid phase microextraction (HS-SPME) GC–MS 5975 C. The mixture was heated at $60\text{ }^{\circ}\text{C}$ and the fiber (50/30 μm DVB/CAR/PDMS) was exposed to the headspace for 30 min. The length of the fiber in the headspace was kept constant. The fiber was exposed to the injector of the gas chromatograph at $250\text{ }^{\circ}\text{C}$. The fiber was left at the port injector for 5 min to remove the contaminants. Helium was used as carrier gas (1 mL/min). Separation of compounds was performed on a DB-Wax column (30 m \times 0.25 mm, $df = 0.25\text{ }\mu\text{m}$, Agilent J&W, USA). The injector, ion source and interface temperatures were set at 250, 200 and $260\text{ }^{\circ}\text{C}$, respectively. The mass spectrometer was operated in the electron impact mode with the electron energy set at 70 eV and scan range 35–400 m/z . Oven temperature was elevated from 40 to $250\text{ }^{\circ}\text{C}$ with a rate of $4\text{ }^{\circ}\text{C}/\text{min}$ 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. The results were performed as the percentage of peak area of specific volatile compound to the area of total identified volatile compounds.

2.4. Statistical analysis

Statistical analysis was conducted using the two-way analysis of variance (ANOVA) with factors such as ultrasound time and thermal treatments; followed by Tukey's post hoc test in Statistica software version 13.5.0.17. Principal component analysis was done for the total amount of group compounds.

3. Results and discussion

3.1. Aldehydes composition of BSG

Aldehyde's composition of BSG treated by bath-ultrasonication and its combination with thermal exposures (conventional water-bath and autoclave treatment) is presented in Table 1. The results demonstrated that volatile compounds on BSG are dominated by aldehydes groups which ranged from 49.1 % to 65.6 %. The influence of bath ultrasonication on the aldehydes fluctuated depending on its combination with autoclave and water-bath thermal treatment. The highest amount of aldehydes was identified in BSG with 25 min bath-ultrasonication incorporated with autoclave treatment. Without thermal exposures, 15 min bath-ultrasonication generated the highest aldehydes ($p < 0.05$) while 5 and 25 min generated the same level of volatile aldehydes ($p > 0.05$). The impact of water-bath treatment depended on time exposure during the bath-ultrasonication. Longer time on bath-ultrasonication generated a higher amount of aldehydes due to the water-bath treatment. The results in Table 1 demonstrated that the fluctuation of the amount of aldehydes occurred due to the reduction and increase as well as the discharge and formation of certain compounds. The study revealed that a number of 22 aldehyde compounds were observed in treated BSG. Some compounds including 3-methyl-butanal, hexanal, (E)-2-octenal, nonanal, (E)-2-nonenal, decanal, (E,E)-2,4-nonadienal, benzaldehyde and benzeneacetaldehyde were present in all treated BSG although with different amounts. Those compounds were also identified

Table 1

Aldehydes compounds of BSG treated with bath ultrasonication and its combination with conventional water bath and autoclave treatments.

Compounds (%)	Bath Ultrasonication								
	5 min			15 min			25 min		
	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath
<i>Butanal, 3-methyl-</i>	4.03 ± 0.01	2.62 ± 0.03	2.88 ± 0.14	2.73 ± 0.18	3.56 ± 0.14	3.09 ± 0.16	2.06 ± 0.05	3.59 ± 0.13	2.92 ± 0.18
<i>Pentanal</i>	–	–	0.30 ± 0.01	0.29 ± 0.00	–	0.69 ± 0.03	–	–	1.14 ± 0.09
<i>Hexanal</i>	20.11 ± 0.67	12.89 ± 0.02	18.21 ± 0.78	13.32 ± 0.49	8.89 ± 0.28	16.14 ± 0.14	16.64 ± 0.47	16.21 ± 0.34	23.20 ± 0.49
<i>2-Hexenal, (E)-</i>	–	–	0.38 ± 0.02	–	–	0.38 ± 0.00	0.62 ± 0.04	–	0.32 ± 0.01
<i>Heptanal</i>	0.45 ± 0.03	0.89 ± 0.01	1.32 ± 0.11	0.79 ± 0.02	0.76 ± 0.00	1.20 ± 0.06	0.52 ± 0.01	–	1.33 ± 0.11
<i>2-Heptenal, (Z)-</i>	0.22 ± 0.02	–	0.24 ± 0.00	–	–	0.94 ± 0.01	–	–	0.38 ± 0.01
<i>2,4-Heptadienal, (E,E)-</i>	–	–	0.30 ± 0.00	0.48 ± 0.00	–	0.40 ± 0.03	–	–	0.47 ± 0.00
<i>Octanal</i>	–	0.31 ± 0.01	–	–	–	–	–	3.13 ± 0.15	–
<i>2-Octenal, (E)-</i>	3.87 ± 0.18	1.40 ± 0.01	2.56 ± 0.10	4.35 ± 0.07	3.29 ± 0.14	3.46 ± 0.22	2.86 ± 0.33	3.88 ± 0.04	3.79 ± 0.08
<i>Nonanal</i>	8.57 ± 0.25	15.54 ± 0.09	8.55 ± 0.08	12.99 ± 0.34	10.30 ± 0.29	10.37 ± 0.03	12.51 ± 0.17	13.43 ± 0.03	6.91 ± 0.37
<i>2-Nonenal, (E)-</i>	2.91 ± 0.16	4.04 ± 0.07	2.52 ± 0.04	6.35 ± 0.29	3.07 ± 0.28	3.08 ± 0.16	3.70 ± 0.38	1.19 ± 0.04	3.19 ± 0.00
<i>Decanal</i>	1.51 ± 0.03	3.26 ± 0.19	2.54 ± 0.05	3.33 ± 0.15	1.68 ± 0.06	2.36 ± 0.15	2.14 ± 0.12	1.34 ± 0.04	1.60 ± 0.11
<i>2-Decenal, (E)-</i>	–	–	–	–	0.40 ± 0.00	–	–	–	–
<i>Undecanal</i>	–	–	0.31 ± 0.01	–	–	0.43 ± 0.01	0.25 ± 0.01	–	–
<i>Dodecanal</i>	–	0.27 ± 0.02	0.74 ± 0.00	–	–	0.36 ± 0.03	0.21 ± 0.00	–	0.12 ± 0.17
<i>7-Hexadecenal, (Z)-</i>	–	–	–	–	0.30 ± 0.01	–	–	–	0.25 ± 0.01
<i>2,4-Decadienal, (E,E)-</i>	–	3.11 ± 0.12	4.17 ± 0.33	3.89 ± 0.15	2.14 ± 0.11	5.03 ± 0.10	0.24 ± 0.01	2.23 ± 0.00	1.30 ± 0.11
<i>2,4-Nonadienal, (E,E)-</i>	0.88 ± 0.03	0.68 ± 0.05	0.56 ± 0.01	1.27 ± 0.02	0.85 ± 0.02	0.97 ± 0.01	0.71 ± 0.09	0.41 ± 0.03	0.76 ± 0.02
<i>Benzaldehyde</i>	3.52 ± 0.18	5.20 ± 0.22	7.16 ± 0.48	0.90 ± 0.05	2.65 ± 0.10	3.85 ± 0.07	2.97 ± 0.09	7.06 ± 0.21	5.19 ± 0.07
<i>Benzeneacetaldehyde</i>	5.60 ± 0.25	7.93 ± 0.14	3.77 ± 0.12	7.06 ± 0.14	11.18 ± 0.18	5.43 ± 0.10	5.81 ± 0.09	13.15 ± 0.08	7.11 ± 0.10
<i>Octadecanal, 2-bromo-</i>	–	1.36 ± 0.06	–	–	–	–	–	–	–
<i>Cyclopentaneacetaldehyde, 2-formyl-3-methyl-α-methylene-</i>	–	0.68 ± 0.02	–	–	–	–	–	–	–
Total*	51.67 ± 0.48^d	60.17 ± 0.03^b	56.53 ± 0.32^c	57.74 ± 0.40^c	49.07 ± 0.76^c	58.17 ± 0.06^c	51.23 ± 0.36^d	65.62 ± 0.13^a	59.97 ± 0.74^b

Note: italic demonstrated its presence in untreated BSG from preliminary study. The percentage is obtained based on the area of the specific compound compared to the total area all identified volatile compounds. The data is shown as mean ± standard deviation from at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$).

in untreated BSG control.

Compared to untreated BSG in our previous study [22], ultrasound continued with autoclave treatment discharged several compounds such as pentanal, (E)-2-hexenal, (Z)-2-heptenal, (E,E)-2,4-heptadienal and undecanal from BSG regardless of time exposure on bath-ultrasonication. Those compounds seem to have pungent, green leaf and pesticide-related odor perception, except undecanal. Pentanal and (Z)-2-heptenal had been identified in BSG which were formed during the fermentation in the brewing process [23,25,26]. Pentanal is responsible for almond, malt and pungent odor perception while (Z)-2-heptenal is responsible for green and pungent [23,25,26]. (E,E)-2,4-Heptadienal and E-2-hexenal have never been observed in BSG. (E)-2-Hexenal was identified as a green leaf volatile which acts as antifungal and is responsible for unpleasant odor in preventing fungi and insects [27] while (E,E)-2,4-heptadienal is a derivative of ascorbic acid which naturally acts as natural flavor for antifungal properties [28]. By this, the presence of (E,E)-2,4-heptadienal and (E)-2-hexenal in untreated BSG might be due to the herbicides treatment during the grain storage before brewing process. Bath-ultrasonication combined with autoclave

treatment has the ability to remove the volatile compounds from post-harvest handling treatments which can be herbicides. This phenomenon has also been reported in vegetables, in which the pesticide residues were removed by ultrasound treatment [29]. Undecanal has a pleasant odor perception which is often found in perfumes [30] which were also removed by the same treatment.

The 5 min bath-ultrasonication combined with autoclave treatment formed 2 compounds including 2-bromo-octanal and 2-formyl-3-methyl-α-methyl-cyclopentyl acetaldehyde which had never been observed in BSG. 2-Formyl-3-methyl-α-methyl-cyclopentyl acetaldehyde had been identified as a volatile compound in medicinal plant [31]. The formation of octanal was induced by the combination of autoclave treatment at 5 min and 25 min bath-ultrasonication while the formation of (E)-2-decenal was observed in the combination of autoclave treatment with 15 min of bath-ultrasonication. Octanal had never been identified in BSG, although it was present in barley and malt [26]. Octanal demonstrated fat, soap, lemon, and green odor perception [23]. The treatment might have reversed the formation of octanal to its original in barley and malt. (E)-2-decenal is a nematocidal compound

which is used to kill parasites [32]. The formation of this compound might be as an impact of the removal of (E,E)-2,4-heptadienal, (E)-2-hexenal and or undecanal as mentioned above. Furthermore, bath-ultrasonication coupled with conventional water-bath treatment had no capability in discharging aldehyde compounds while it was capable of forming dodecanal. Dodecanal may be synthesized from dodecanol by dehydrogenation [30] which demonstrated citrus oil odor perception. The presence and absence of other aldehydes compounds fluctuated irrespective of bath ultrasonication and thermal exposure.

The tendency of bath-ultrasonication in discharging and or forming volatile aldehyde compounds in BSG seemed to be depending on the thermal exposure. Combination with autoclave treatment tended to modify the aldehydes volatile by replacing certain compounds while conventional water-bath tended to generate the same volatile profile as it was in untreated BSG. In contrast, our preliminary results revealed that conventional water-bath degraded the amount of aldehyde compounds while autoclave treatment tended to intensify aldehyde volatiles quantitatively. Furthermore, conventional water-bath had a higher tendency in discharging aldehyde volatile compounds compared to autoclave treatment. This phenomenon might explain the different degradation mechanism of bath-ultrasonication on aldehyde volatiles of BSG. A previous study emphasized that the impact of ultrasonication depends on its combination with certain techniques, power used, solvent used and solvent ratio [1]. The combination of ultrasound with thermal exposure and pressure might act synergistically [19] thus modifying the volatile aldehydes of BSG.

3.2. Ketones

The impact of bath-ultrasonication and its combination with conventional water-bath and autoclave treatment on volatile ketones of BSG is shown in Table 2. The results showed that bath-ultrasonication at different levels of time exposure had no significant effect ($p > 0.05$) on the amount of ketone volatiles. The higher amount of volatile ketones was identified in BSG treated with bath-ultrasonication without thermal

exposure followed by its combination with conventional water-bath and autoclave treatment. The combination of thermal exposures with bath-ultrasonication significantly ($p < 0.05$) decreased the amount of volatile ketones from a range of 9.5%–10.6% to a range of 7.7%–8.6% and 4.6%–5.6% for conventional water-bath and autoclave treatment, respectively. This phenomenon demonstrated that the degradation in volatile ketones might be caused by the level exposure of temperature. (E,E)-3,5-Octadien-2-one was the only ketone which was present in all treated BSG including in untreated BSG. It shows its resistance to ultrasonication and thermal exposure. (E,E)-3,5-Octadien-2-one was identified in cereal grain [33] which was responsible for stale odor in tea and chestnut-like odor perception [34,35].

6-Methyl-5-hepten-2-one and 2-methyl-3-octanone were identified in fresh untreated BSG while it only occurred in conventional water-bath at 5 min and 15 min, respectively. The majority of the treatments removed 6-methyl-5-hepten-2-one and 2-methyl-3-octanone from BSG. 6-Methyl-5-hepten-2-one was reported for being responsible for herb, oily, pungent, pear, pepper, and mushroom odor perception [23], and has been reported to be present in cereal grains [33] and BSG-added crackers [36] and grain malts [23]. 2-Methyl-3-octanone was present in processed meat products [37] which might be responsible for meat-related odor perception.

The formation of certain volatile ketones due to bath-ultrasonication and its combination with thermal treatments was also observed including 2-undecanone, 5-methyl-2-hexanone, 6-(hydroxy-phenyl-methyl)-2,2-dimethyl-cyclohexanone, 4,4-diethyl-spiro[2.3]hexan-5-one, and 1-(2,2-dimethylcyclopentyl)-ethanone. Those compounds had never been reported in BSG. 2-Undecanone and 6-(hydroxy-phenyl-methyl)-2,2-dimethyl-cyclohexanone was present in milk and fermented chickpea milk respectively [38,39]. 5-Methyl-2-hexanone has been reported in black tea [40] and 4,4-diethyl-spiro[2.3]hexan-5-one was identified in green tea [41]. Furthermore, 1-(2,2-dimethylcyclopentyl)-ethanone was observed in marine salt [42]. The formation of those compounds might intensify the milky and tea odor perception.

Our preliminary studies demonstrated that autoclave reduced the

Table 2

Ketones compounds of BSG treated with bath ultrasonication and its combination with conventional water bath and autoclave treatments.

Compounds (%)	Bath Ultrasonication								
	5 min			15 min			25 min		
	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath
<i>3,5-Octadien-2-one, (E,E)-</i>	7.57 ± 0.54	2.38 ± 0.49	4.57 ± 0.27	7.07 ± 0.47	4.51 ± 0.19	4.66 ± 0.34	7.04 ± 0.28	2.79 ± 0.05	5.13 ± 0.06
<i>2-Heptanone</i>	0.40 ± 0.01	0.48 ± 0.01	0.54 ± 0.01	0.84 ± 0.00	–	0.87 ± 0.00	0.51 ± 0.03	0.97 ± 0.05	1.21 ± 0.04
<i>3-Octen-2-one, (E)-</i>	0.52 ± 0.02	–	–	0.86 ± 0.04	–	0.60 ± 0.01	0.98 ± 0.00	0.82 ± 0.05	1.97 ± 0.04
<i>5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-</i>	0.22 ± 0.01	0.65 ± 0.09	0.28 ± 0.01	–	0.31 ± 0.01	0.40 ± 0.03	0.51 ± 0.01	–	–
<i>2-Undecanone</i>	–	1.56 ± 0.01	1.28 ± 0.01	1.20 ± 0.01	–	0.75 ± 0.03	0.45 ± 0.02	–	–
<i>2-Hexanone, 5-methyl-</i>	0.32 ± 0.01	–	0.71 ± 0.06	–	0.72 ± 0.01	0.29 ± 0.00	–	–	–
<i>6-(Hydroxy-phenyl-methyl)-2,2-dimethyl-cyclohexanone</i>	0.98 ± 0.03	–	–	–	–	–	–	–	–
<i>Spiro[2.3]hexan-5-one, 4,4-diethyl-</i>	–	–	0.46 ± 0.02	–	–	–	–	–	–
<i>5-Hepten-2-one, 6-methyl-</i>	–	–	0.24 ± 0.01	–	–	–	–	–	–
<i>Ethanone, 1-(2,2-dimethylcyclopentyl)-</i>	–	–	–	0.60 ± 0.02	–	–	–	–	0.34 ± 0.03
<i>3-Octanone, 2-methyl-</i>	–	–	–	–	–	0.17 ± 0.00	–	–	–
Total*	10.00 ± 0.58^a	5.06 ± 0.41^d	8.08 ± 0.21^c	10.56 ± 0.43^a	5.55 ± 0.16^d	7.74 ± 0.27^c	9.51 ± 0.23^{ab}	4.58 ± 0.25^d	8.64 ± 0.05^{bc}

Note: italic demonstrated its presence in untreated BSG from preliminary study. The percentage is obtained based on the area of the specific compound compared to the total area all identified volatile compounds. The data is shown as mean ± standard deviation from at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$).

amount of volatile ketones [22], while water-bath increased and/or at least generated the same level as in untreated BSG (Unpublished data). However, the incorporation of water-bath and autoclave treatment in the current study lowered the amount of volatile ketones. The results demonstrated that methyl ketones which were present in untreated BSG were discharged. At the same time, the formation of other methyl ketones was identified. The discharged methyl ketones might be due to its conversion to the newly identified methyl ketones. Methyl ketones predominantly originate in the lipid fraction [38]. The discharging and formation of methyl ketones shows the instability of lipid fraction in BSG due to bath-ultrasonication and its combination with thermal exposure. The modification of lipid fraction due to ultrasonication had been

reported previously [1]. Moreover, the alteration of chemical composition and chemical reaction might occur due to the physical forces in the solution as discovered previously [19].

3.3. Alcohols

Volatile alcohol composition of treated BSG is presented in Table 3. In general, bath-ultrasonication combined with thermal exposure reduced the amount of alcohol, except 15 min bath ultrasonication. The results revealed that the majority of observed alcohols in untreated BSG were eliminated by the majority of the treatment, except 1-octen-3-ol which was identified in all groups treated BSG. (Z)-2-Octen-1-ol were

Table 3

Alcohol compounds of BSG treated with bath ultrasonication and its combination with conventional water bath and autoclave treatments.

Compounds (%)	Bath-ultrasonication								
	5 min			15 min			25 min		
	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath
<i>1-Octen-3-ol</i>	1.42 ± 0.02	0.69 ± 0.01	1.23 ± 0.01	0.95 ± 0.00	1.15 ± 0.08	1.55 ± 0.05	1.71 ± 0.00	1.12 ± 0.05	2.86 ± 0.07
3,5-Octadien-2-ol	0.86 ± 0.05	0.35 ± 0.00	0.88 ± 0.01	0.58 ± 0.00	1.10 ± 0.03	0.63 ± 0.03	–	0.84 ± 0.01	–
1-Pentanol	0.40 ± 0.01	–	0.54 ± 0.02	0.82 ± 0.00	–	0.86 ± 0.01	0.54 ± 0.00	–	1.17 ± 0.04
<i>2-Octen-1-ol, (Z)-</i>	0.42 ± 0.00	–	0.34 ± 0.02	0.40 ± 0.02	0.28 ± 0.01	0.49 ± 0.01	0.40 ± 0.00	–	0.34 ± 0.02
<i>1-Hexadecanol</i>	1.49 ± 0.01	0.32 ± 0.01	0.82 ± 0.01	–	0.99 ± 0.01	0.48 ± 0.02	1.35 ± 0.10	–	–
<i>Nona-3,5-dien-2-ol</i>	0.49 ± 0.01	–	0.23 ± 0.01	–	–	–	0.31 ± 0.02	–	–
<i>2-Butyl-2,7-octadien-1-ol</i>	0.51 ± 0.02	–	–	–	–	0.36 ± 0.03	0.64 ± 0.01	–	–
2-Decen-1-ol, (E)-	0.74 ± 0.03	–	–	–	–	–	0.27 ± 0.03	–	–
Bicyclo[2.2.2]octan-1-ol, 2-methyl-	1.15 ± 0.02	–	–	–	–	–	0.87 ± 0.02	–	–
2-Heptyn-1-ol	0.26 ± 0.01	–	–	–	–	–	–	–	–
Behenic alcohol	0.40 ± 0.02	–	–	–	–	–	–	–	–
1-Hexanol, 2-ethyl- <i>n</i> -Heptadecanol-1	–	1.00 ± 0.01	–	–	0.59 ± 0.01	–	–	–	–
Ethanol, 2-phenoxy-	–	0.32 ± 0.01	–	–	–	–	0.72 ± 0.01	–	–
(3-Methyl-oxiran-2-yl)-methanol	–	0.50 ± 0.01	–	–	–	–	–	–	–
<i>1-Tetradecanol</i>	–	–	0.55 ± 0.01	–	0.35 ± 0.00	0.20 ± 0.00	0.49 ± 0.01	–	–
<i>4,4,6-Trimethyl-cyclohex-2-en-1-ol</i>	–	–	0.57 ± 0.01	–	0.57 ± 0.04	1.00 ± 0.05	1.20 ± 0.09	–	–
1-Decanol, 2-hexyl-	–	–	0.83 ± 0.01	–	–	1.19 ± 0.04	–	–	–
<i>n</i> -Tridecan-1-ol	–	–	0.28 ± 0.00	–	–	–	–	–	–
Bicyclo[3.1.1]hept-3-en-2-ol, 4,6,6-trimethyl-	–	–	0.37 ± 0.01	–	–	–	–	–	–
Cyclohexanol, 1-methyl-4-(1-methyl-phenyl)-, acetate	–	–	–	0.45 ± 0.02	–	0.27 ± 0.00	–	–	–
1-Hexanol	–	–	–	–	–	0.26 ± 0.00	0.22 ± 0.01	–	0.31 ± 0.01
<i>2-Nitrohept-2-en-1-ol</i>	–	–	–	–	–	0.20 ± 0.00	0.56 ± 0.02	–	–
9-Oxabicyclo[6.1.0]nonan-4-ol	–	–	–	–	–	0.25 ± 0.00	–	–	–
<i>trans</i> -2-Undecen-1-ol	–	–	–	–	–	–	0.24 ± 0.01	–	–
Bicyclo[3.3.1]nonane-2,6-diol	–	–	–	–	–	–	–	0.38 ± 0.03	–
Total*	8.14 ± 0.18^b	3.58 ± 0.04^c	6.64 ± 0.04^c	3.20 ± 0.04^c	5.02 ± 0.11^d	7.97 ± 0.13^b	9.53 ± 0.32^a	2.34 ± 0.00^f	4.68 ± 0.06^d

Note: italic demonstrated its presence in untreated BSG from preliminary study. The percentage is obtained based on the area of the specific compound compared to the total area all identified volatile compounds. The data is shown as mean ± standard deviation from at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$).

eliminated by bath-ultrasonication combined with autoclave at 5 and 25 min while it was present in other treatments. 1-Hexadecanol was mostly discharged by 25 min bath ultrasonication combined with both autoclave and water-bath treatment. This phenomenon explains that the most stable compound after the treatments with bath-ultrasonication and its combination with thermal exposures was 1-octen-3-ols followed by (Z)-2-octen-1-ol and 1-hexadecanol. 1-Octen-3-ols is commonly discovered as volatile metabolites in cereal grain [33] which

represented mushroom odor perception [26]. However, (Z)-2-octen-1-ol and 1-hexadecanol had never been identified in BSG. (Z)-2-Octen-1-ol was present in fermented liquor [43] and 1-hexadecanol is a fatty alcohol [44] which acts as a lubricant in cosmetics. Other alcohol compounds observed in untreated BSG were most likely to be unstable and removed due to the treatments such as nona-3,5-dien-2-ol, 2-butyl-2,7-octadien-1-ol, 1-tetradecanol, 4,4,6-trimethyl-cyclohex-2-en-1-ol and 2-nitrohept-2-en-1-ol. All those compounds were identified in

Table 4

Alkanes compounds of BSG treated with bath ultrasonication and its combination with conventional water bath and autoclave treatments.

Compounds (%)	Bath Ultrasonication								
	5 min			15 min			25 min		
	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath
<i>Dodecane</i>	6.04 ± 0.01	4.46 ± 0.04	1.88 ± 0.00	3.68 ± 0.04	8.75 ± 0.44	3.48 ± 0.04	3.92 ± 0.05	4.74 ± 0.14	4.43 ± 0.00
<i>Tridecane</i>	5.86 ± 0.05	6.15 ± 0.26	5.13 ± 0.50	5.14 ± 0.04	7.03 ± 0.28	5.00 ± 0.10	5.31 ± 0.15	5.41 ± 0.11	4.24 ± 0.00
<i>Tetradecane</i>	1.16 ± 0.04	2.18 ± 0.02	1.73 ± 0.07	1.17 ± 0.04	2.26 ± 0.00	0.58 ± 0.01	1.72 ± 0.00	0.78 ± 0.05	0.26 ± 0.00
1-Pentadecene	0.80 ± 0.02	1.89 ± 0.07	1.71 ± 0.05	1.89 ± 0.04	0.99 ± 0.01	0.58 ± 0.01	1.57 ± 0.04	0.59 ± 0.02	0.25 ± 0.00
<i>Tetradecane, 2,6,10-trimethyl-</i>	0.79 ± 0.07	1.77 ± 0.03	1.21 ± 0.05	1.86 ± 0.04	2.11 ± 0.06	0.97 ± 0.02	2.50 ± 0.18	–	–
Cyclopentane, undecyl-	0.25 ± 0.01	0.76 ± 0.01	0.32 ± 0.01	0.45 ± 0.04	0.72 ± 0.01	0.31 ± 0.00	0.66 ± 0.03	–	–
1-Tridecene	0.36 ± 0.01	0.35 ± 0.00	–	0.27 ± 0.04	0.43 ± 0.00	0.49 ± 0.01	0.28 ± 0.00	–	–
<i>n</i> -Nonylcyclohexane	0.40 ± 0.01	1.10 ± 0.02	0.48 ± 0.00	–	–	0.34 ± 0.00	0.45 ± 0.01	–	–
3-Trifluoroacetoxytetradecane	0.43 ± 0.01	0.29 ± 0.00	–	–	–	0.20 ± 0.00	–	–	–
1,2–15,16-Diepoxyhexadecane	0.29 ± 0.01	0.36 ± 0.00	–	–	0.33 ± 0.00	0.21 ± 0.00	–	–	–
Undecane	0.91 ± 0.03	–	–	–	0.75 ± 0.05	–	–	0.50 ± 0.04	0.24 ± 0.00
1,2–15,16-Diepoxyhexadecane	0.47 ± 0.03	–	0.46 ± 0.00	–	0.46 ± 0.01	–	0.47 ± 0.01	0.70 ± 0.02	0.65 ± 0.00
2-Tridecene, (Z)-	0.37 ± 0.01	–	–	–	0.38 ± 0.00	–	–	0.53 ± 0.05	0.38 ± 0.00
Eicosane, 2-cyclohexyl-	0.42 ± 0.02	–	0.46 ± 0.01	0.59 ± 0.04	0.36 ± 0.00	–	–	–	–
Cyclohexene, 3-(3-methyl-1-butanyl)-, (E)-	0.34 ± 0.01	–	–	–	–	–	–	–	–
Heptylcyclohexane	0.23 ± 0.02	–	–	–	–	–	–	–	–
1-Tetradecene	–	0.28 ± 0.01	–	–	0.34 ± 0.00	–	–	–	–
<i>Nonadecane</i>	–	0.37 ± 0.00	0.27 ± 0.01	0.66 ± 0.04	0.35 ± 0.00	0.21 ± 0.00	0.56 ± 0.01	–	–
Hexadecane, 1,1-bis(dodecyloxy)-	–	–	–	1.12 ± 0.04	–	–	0.22 ± 0.01	–	–
7-Hexadecene, (Z)-	–	–	–	–	–	–	0.28 ± 0.02	–	–
4-Trifluoroacetoxy pentadecane	–	–	–	–	–	0.50 ± 0.00	–	–	–
1-Eicosene	–	–	–	–	–	0.16 ± 0.01	–	–	–
Cyclododecane	–	–	0.60 ± 0.00	–	–	–	–	–	–
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	–	–	–	0.35 ± 0.04	–	0.82 ± 0.03	–	–	–
Octadecane, 6-methyl-	–	–	–	–	–	0.18 ± 0.01	–	–	–
1-Docosene	–	–	–	0.26 ± 0.04	–	–	–	–	–
1-Hexacosene	–	–	–	0.26 ± 0.04	–	0.40 ± 0.02	0.22 ± 0.01	–	–
17-Pentatriacontene	–	–	–	–	1.01 ± 0.00	–	0.52 ± 0.01	–	–
2-Methyl-E-7-hexadecene	–	–	–	–	–	0.18 ± 0.01	–	–	–
Total*	19.12 ± 0.19^{bc}	19.97 ± 0.46^b	14.25 ± 0.29^d	17.69 ± 0.35^c	26.26 ± 0.76^a	14.62 ± 0.20^d	18.68 ± 0.10^{bc}	13.25 ± 0.43^d	10.44 ± 0.31^e

Note: italic demonstrated its presence in untreated BSG from preliminary study. The percentage is obtained based on the area of the specific compound compared to the total area all identified volatile compounds. The data is shown as mean ± standard deviation from at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$).

medicinal plants and or essential oil [45–50].

The formation of alcohol compounds occurred in several treatments. 3,5-Octadien-2-ol was formed in almost all treated BSGs except at 25 min bath ultrasonication and its combination with water-bath treatment. 1-Pentanol was formed except in autoclaved combination treatment. (E)-2-Decen-1-ol and 2-methyl-bicyclo[2.2.2]octan-1-ol were formed by bath-ultrasonication at 5 and 25 min. Furthermore, certain compounds were formed when only combined with thermal exposure such as 2-ethyl-1-hexanol, *n*-heptadecanol-1, (3-methyl-oxiran-2-yl)-methanol, 2-hexyl-1-decanol, *n*-tridecan-1-ol, 4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-ol, 9-oxabicyclo[6.1.0]nonan-4-ol, and bicyclo[3.3.1]nonane-2,6-diol. 2-ethyl-1-hexanol had been identified in grain [33,51], which is responsible for a resin, flower, and green odor perception [23]. Other compounds had never been observed in BSG while it commonly occurs in essential oil and or leaves extracts [52–59]. The modification of alcohol profiles might be due to the degradation of polysaccharides as an impact of the treatments. Acoustic cavitation causes disintegration of solid materials and disruption of cell walls allowing the mass transfer from solid matrix to the solution [19].

3.4. Alkanes

The composition of volatile alkanes is presented in Table 4. Alkanes stood as the second highest volatile group in BSG which ranged from

10.44 % to 26.26 %. The results demonstrated that time exposure on bath-ultrasonication had no significant difference ($p > 0.05$) on the amount of volatile alkanes. However, its combination with thermal exposures (conventional water-bath and autoclave treatment) significantly ($p < 0.05$) fluctuated the volatile alkanes. Combination of bath-ultrasonication with conventional water-bath treatment generated the lowest amount of volatile alkanes at a range of 10.44 %–14.25 %. There are 4 compounds which seem to be the most stable during the treatments by their presence in all treated BSG such as dodecane, tridecane, tetradecane and 1-pentadecene. The occurrence of 1-pentadecene was not observed in untreated BSG; while dodecane, tridecane and tetradecane had been identified in its origin untreated BSG. Dodecane and tetradecane had been reported to be present in cereal grains [33] while tridecane and 1-pentadecane had never been identified in BSG.

The majority of the treatments formed several compounds including undecyl-cyclopentane, 1-tridecene, *n*-nonylcyclohexane, 1,2-15,16-diepoxyhexadecane and nonadecane which were not discovered on untreated BSG. 1-tridecene was identified in stored wheat [60]; *n*-nonylcyclohexane occurred due to the high thermal exposure on cellulose and or lignin [61]; nonadecane acted as host attractions in flowers [62]; while undecyl-cyclopentane and 1,2-15,16-diepoxyhexadecane had been reported in medicinal plants [63,64]. Moreover, several compounds were also formed by certain treatments (Table 1). The formation of new volatile alkanes shows a modification in the volatile profile of

Table 5

Fatty acids compounds of BSG treated with bath ultrasonication and its combination with conventional water bath and autoclave treatments.

Compounds (%)	Bath ultrasonication								
	5 min			15 min			25 min		
	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath
<i>Hexanoic acid</i>	0.26 ± 0.03	–	–	–	–	0.83 ± 0.00	–	–	–
<i>n</i> -Hexadecanoic acid	1.18 ± 0.06	2.14 ± 0.11	4.67 ± 0.08	2.12 ± 0.10	2.58 ± 0.07	1.16 ± 0.06	0.38 ± 0.00	1.40 ± 0.01	–
Dichloroacetic acid, tridecyl ester	0.37 ± 0.01	0.96 ± 0.02	–	–	–	–	–	–	–
[1,1'-Bicyclopropyl]-2-octanoic acid, 2'-hexyl-, methyl ester	0.21 ± 0.03	–	–	–	–	–	–	–	–
Nonanoic acid	–	1.55 ± 0.05	0.95 ± 0.09	0.81 ± 0.00	1.17 ± 0.04	0.53 ± 0.01	0.57 ± 0.01	–	–
Pentanoic acid	–	0.48 ± 0.01	–	–	0.69 ± 0.01	–	–	0.67 ± 0.04	0.99 ± 0.06
Tetradecanoic acid	–	0.32 ± 0.01	0.62 ± 0.00	–	0.37 ± 0.00	–	–	–	–
Oleic acid	–	0.29 ± 0.01	–	–	–	–	–	–	–
Hexanoic acid, 1-cyclopentylethyl ester	–	–	0.45 ± 0.01	–	0.60 ± 0.01	–	–	0.41 ± 0.02	1.19 ± 0.03
9-Hexadecenoic acid	–	–	0.24 ± 0.01	–	–	–	–	–	–
Pentanoic acid, 2,2,4-trimethyl-3-carboxyisopropyl, isobutyl ester	–	–	–	–	–	0.80 ± 0.04	–	–	–
Pentadecanoic acid	–	–	0.31 ± 0.00	–	–	–	–	–	–
Octanoic acid	–	–	–	0.55 ± 0.01	–	0.22 ± 0.02	–	–	–
<i>n</i> -nonylcyclohexane	–	–	–	0.59 ± 0.01	–	–	–	–	–
Docosanoic acid, 1,2,3-propanetriyl ester	–	–	–	0.59 ± 0.01	2.04 ± 0.00	–	–	–	–
Dodecanoic acid, 3-hydroxy-	–	–	–	–	–	–	0.50 ± 0.00	–	–
<i>trans</i> -2-undecenoic acid	–	–	–	–	–	–	–	0.42 ± 0.01	0.33 ± 0.01
Dichloroacetic acid, tetradecyl ester	–	–	–	–	–	–	–	0.62 ± 0.04	0.88 ± 0.02
Total*	2.03 ± 0.11^f	5.73 ± 0.05^c	7.25 ± 0.14^b	4.08 ± 0.09^d	7.36 ± 0.01^a	3.54 ± 0.01^e	1.45 ± 0.01^g	3.52 ± 0.12^e	3.39 ± 0.08^e

Note: italic demonstrated its presence in untreated BSG from preliminary study. The percentage is obtained based on the area of the specific compound compared to the total area all identified volatile compounds. The data is shown as mean ± standard deviation from at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$).

treated BSG. From the perspective of food processing and acceptability, this modification might improve the BSG-added products due to the masking ability of new compounds which masked undesired odor perception.

3.5. Fatty acids

The profile of fatty acid volatiles of BSG treated by bath-ultrasonication and its combination with conventional water-bath and autoclave treatment is presented in Table 5. In general, combination of thermal exposure with bath-ultrasonication intensified the total amount of volatile fatty acids except 15 min bath-ultrasonication combined with autoclave which significantly ($p < 0.05$) decreased. Bath-ultrasonication with no thermal combination generated a range of 1.45 % to 4.08 % volatile fatty acids. While its combination with conventional water-bath and autoclave generated at a range of 3.39 % to 7.36 %. According to our preliminary study, only hexanoic acid was observed in untreated dried BSG. Our current study demonstrated that hexanoic acid only existed in 2 treatments including bath-ultrasonication at 5 min and combination of 15 min bath-ultrasonication with conventional water-bath treatment. By this, the majority of bath-ultrasonication and its combination with thermal exposure eliminated the presence of hexanoic acid. Hexanoic acid was formed due to the malting process in the brewery industry and this compound is responsible for sweaty odor perception [23]. The ability of studied treatments in eliminating sweaty perception might benefit further valorisation of BSG, particularly from the food acceptability point of view.

There are a number of 17 new volatile fatty acids which were formed due to the treatments. This phenomenon demonstrated that bath-ultrasonication combined with autoclave and conventional water-bath treatment significantly modified the volatile fatty acid composition of BSG. The results showed that the majority of the treatments induced the formation of *n*-hexadecanoic acid and nonanoic acid. *N*-hexadecanoic acid has been reported for its role in fruit juice [65] and nonanoic acid was present in cereal grain [33]. A number of 6 of newly formed compounds were fatty acid ester which tended to demonstrate fruity odor perception, including tridecyl ester dichloroacetic acid, methyl ester 2'-hexyl-[1,1'-Bicyclopropyl]-2-octanoic acid, 1-cyclopentyl ethyl ester hexanoic acid, isobutyl ester pentanoic acid, 2,2,4-trimethyl-3-carboxyisopropyl, 1,2,3-propanetriyl ester docosanoic acid, and tetradecyl ester dichloroacetic acid. As mentioned above that bath-ultrasonication and

its combination with autoclave and conventional water-bath eliminated sweaty odor perception and at the same time it produced fatty acid compounds which are responsible for the fruity and grainy. The modification in volatile fatty acids might be related to its modification in lipid profile because ultrasound treatment can lead to the modification of lipid composition and degradation [1]. It was emphasized that high temperatures in cavitation bubbles due to the ultrasound may induce the formation of rancid, burnt and off-flavors compounds, as an impact of lipid oxidation [16]. Current study seems to demonstrate a contrast phenomenon, in which unpleasant (sweaty perception) compounds were discharged and the pleasant odors (fruity and grainy) were formed. By this, a synergistic impact between ultrasound treatment continued with water-bath and autoclave heating might have occurred.

3.6. Furans and other compounds

The profile of volatile furan compositions of treated BSG is presented in Table 6. The results showed that the amount of volatile furans was slightly different ($p < 0.05$) among the groups. In general, bath-ultrasonication combined with autoclave treatment had the lowest level of total amount of volatile furans. A total of 4 furan compounds were identified including 2-pentyl-furan, 5-heptyldihydro-2(3H)-furanone, furfural and tetrahydro-2-(12-pentadecynyl)-2H-pyran. 2-pentyl-furan has been identified in untreated fresh BSG (unpublished data) while 5-heptyldihydro-2(3H)-furanone, furfural and tetrahydro-2-(12-pentadecynyl)-2H-pyran was absent in untreated BSG. This phenomenon shows the ability of bath-ultrasonication and its combination with thermal exposures in forming those compounds. Current study revealed that 2-pentyl-furan was present in all treatments. This phenomenon shows its stability during bath-ultrasonication and its combination with conventional water-bath and autoclave treatment. 2-pentyl-furan was reported to be present in BSG [26] due to the Maillard reaction during the malting process [23,25]. This compound was responsible for green bean, fruity, and butter odor perception [23,36]. Furfural had never been reported in BSG while its presence in BSG-added snacks and crackers had been identified [25,36] which represented sweet and almond odor perception [25]. Moreover, 5-heptyldihydro-2(3H)-furanone and tetrahydro-2-(12-pentadecynyl)-2H-pyran had never been reported in BSG. Both compounds demonstrated apricot-like perception and resinous odor perception, respectively [66–68]. By this, bath-ultrasonication as well as its association with conventional

Table 6

Furan and other compounds of BSG treated with bath ultrasonication and its combination with conventional water bath and autoclave treatments.

Compounds (%)	Bath Ultrasonication								
	5 min			15 min			25 min		
	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath	Control	Autoclaved	Water-bath
<i>Furan, 2-pentyl-</i>	7.47 ± 0.67	4.83 ± 0.03	5.67 ± 0.02	5.26 ± 0.29	4.42 ± 0.04	6.05 ± 0.19	7.70 ± 0.32	7.46 ± 0.36	11.03 ± 0.22
2(3H)-Furanone, 5-heptyldihydro-	0.71 ± 0.00	0.65 ± 0.03	0.54 ± 0.04	0.32 ± 0.02	–	0.59 ± 0.02	0.76 ± 0.05	–	–
Furfural	–	–	0.73 ± 0.00	0.62 ± 0.03	0.74 ± 0.00	1.32 ± 0.03	0.50 ± 0.00	0.49 ± 0.01	0.61 ± 0.01
2H-Pyran, tetrahydro-2-(12-pentadecynyl)-	–	–	–	–	0.30 ± 0.01	–	–	–	–
Total*	8.18 ± 0.67^{bc}	5.48 ± 0.01^e	6.94 ± 0.06^{cd}	6.19 ± 0.33^{de}	5.47 ± 0.02^f	7.96 ± 0.13^{bc}	8.96 ± 0.37^b	7.95 ± 0.35^{bc}	11.64 ± 0.23^a
Other									
D-Limonene	0.85 ± 0.09	–	–	0.28 ± 0.01	0.89 ± 0.03	–	0.42 ± 0.00	2.74 ± 0.09	1.23 ± 0.03
Benzene, 1-methyl-3-(1-methylethyl)-	–	–	0.32 ± 0.01	0.25 ± 0.00	–	–	–	–	–
1R- α -Pinene	–	–	–	–	–	–	0.23 ± 0.01	–	–

Note: italic demonstrated its presence in untreated BSG from preliminary study. The percentage is obtained based on the area of the specific compound compared to the total area all identified volatile compounds. The data is shown as mean ± standard deviation from at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$).

water-bath and autoclave treatment were able to form furan compounds which might improve the desirability of BSG.

Furthermore, other compounds including α -limonene, 1R-alpha-pinene, and 1-methyl-3-(1-methylethyl)-benzene were observed to be present due to the several treatments. α -limonene, which was present in untreated BSG, occurred in the majority of the treatments. α -limonene was identified in cereal grain [33] and in BSG which represented citrus and mint odor perception [26]. Meanwhile, 1R- α -pinene and 1-methyl-3-(1-methylethyl)-benzene were absent in untreated BSG. These compounds had never been reported to be present in BSG. Their presence was reported in ginger [69].

The modification of volatile compounds might occur in synergistic mechanisms. An excellent review emphasized that ultrasound in liquid generates physical forces which include microjets, shear forces, shock waves and turbulence which alter the chemical reaction and composition [1,19]. Depolymerisation of polysaccharides occurred as a recombination of radicals formed in saccharides and aromatic components which consequently intensified the water-soluble xylans from corn hull [70]. Sonochemical degradation in chitosan and starch has also been observed due to the formation of OH-radicals combined to mechanochemical effects [70]. Moreover, ultrasound has been successfully used to remove lignin and intensify cellulose and hemicellulose from lignocellulosic in spent coffee waste [2]. The current study was conducted on semi-solid sludge in which the BSG was not completely solubilized. Acoustic cavitation causes disintegration of solid materials and disruption of cell walls allowing the mass transfer from solid matrix to the water fractions [1,19]. Therefore, a complete phenomenon might have occurred including physical forces in the water fraction as well as disintegration of BSG matrix. Furthermore, the modification of volatile compounds was altered by the thermal exposure which degraded polysaccharides in BSG as reported previously [20,21].

3.7. Principle component analysis (PCA)

As is shown in Fig. 1, PCA demonstrated that bath-ultrasonication without thermal treatments influenced the profile of ketones and alcohols composition, regardless of time elevation during bath-ultrasonication. Combination of bath-ultrasonication at 25 min with water-bath treatment seems to be related to the alteration of volatile furans. 5 min and 15 min bath-ultrasonication without thermal

treatment was responsible for alkanes. Furthermore, the total amount of volatile fatty acids seems to be due to the autoclave treatment. The results demonstrated that time elevation on bath-ultrasonication modified the volatile compounds depending on the further thermal exposure. Furthermore, a synergistic action between bath-ultrasonication and thermal exposures which depend on temperature level. This phenomenon has been reported previously [19,71]. The modification in volatile compounds of BSG demonstrated the modification of odor perception which might influence the sensory acceptability of BSG-added food products. As mentioned in previous sections, aldehydes compounds which are responsible for pungent, green leaf and pesticide-related odor perception were eliminated. However, the formation of sweet, fruity, milky and flowers in ketones, alcohols, alkanes, fatty acids and furans groups was also identified. From the perspective of food processing and acceptability, this modification might improve the BSG-added products due to the reformation of volatile compounds.

The modification of volatile compounds might also be an impact of oxidation associated with cavitation (sonolysis). Cavitation can break water molecules and form free radicals (hydroxide radicals and hydrogen atoms) which consequently accelerate the chemical degradation [15]. It was highlighted that the formation of free radicals may or may not be beneficial. The alteration of volatile composition of BSG due to the ultrasound might have occurred due to depolymerisation by two possible mechanisms including chemical degradation and mechanical degradation as emphasized in a previous study [14]. Those mechanisms might be influenced by both cavitation from sound waves and thermal exposure from water-bath and autoclave heating. The alteration of certain volatile compounds vary depending on their stability to the cavitation and/or thermal treatments. Some compounds were removed showing its low resistance to the formed hydroxyl free radical. The showed that volatile fatty acids seems to be the most highly affected by cavitation; aldehydes, alcohols, and furans depended on its combination with thermal exposure; while ketones and alkanes are highly influenced by thermal treatments. The alteration of those volatile compositions of BSG might have been followed by the disruption of dietary fiber due to the ultrasound treatment. Severe fractural change of dietary fiber was identified in palm-pressed fiber treated with 30 min ultrasound. This observation led to a conclusion that cavitation disrupted the vegetal cell wall [72]. BSG is a complex material which is dominated by insoluble dietary fiber. Ultrasound on BSG might have increased the accessibility

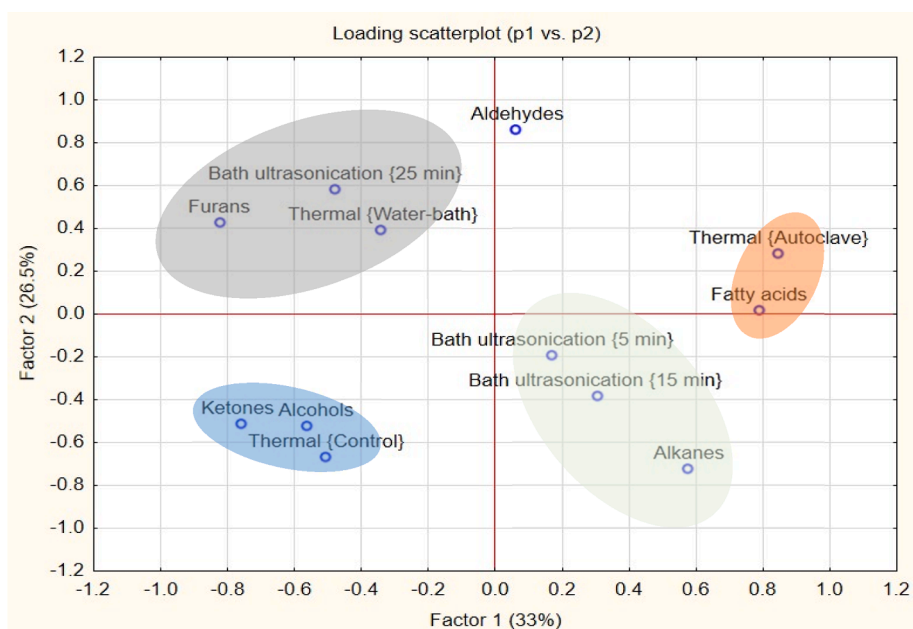


Fig. 1. Principle component analyses of volatile composition of bath-type ultrasonics treated BSG.

of cellulose and decreased the hydrophobicity of crystalline cellulose as previously observed [17].

4. Conclusion

Bath-ultrasonication as well as its combination with thermal exposures (conventional water-bath and autoclave treatment) modified the volatile compositions of BSG. Bath-ultrasound allowed the physical forces in water fraction and sonochemical modification in BSG fraction in the mixture. Thermal exposures allowed disintegration of polysaccharides and fluctuated the volatile profiles of BSG. As the impact of physical forces and polysaccharides degradation, the treatments eliminated and at the same time induced the formation of certain compounds. As a consequence, the treatments are seemingly able to intensify the desirable odor perception and mask the undesirable one. In addition to the possibility of masking and renewing the odor perception of BSG, it is important to emphasize that the treatments were able to remove volatile compounds ((E,E)-2,4-heptadienal and (E)-2-hexenal) which might occur due to the post-harvest or storage treatment such as herbicidal treatment. Furthermore, bath-ultrasonication combined with autoclave treatment tended to modify the composition of volatile aldehydes while its combination with conventional water-bath generated the same aldehyde profile as it was in untreated BSG. Time exposure on bath-ultrasonication had no significant influence on the amount of ketones and alkanes compounds, while the fluctuation occurred as an impact of thermal exposures. Furthermore, the treatment reduced the amount of alcohol and increased the fatty acids. Further investigation in olfactory odor perception, chemical constituents and biological properties is seemingly important.

CRedit authorship contribution statement

Joncser Naibaho: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Funding acquisition. **Anna Pudło:** Methodology, Validation, Investigation, Resources, Writing – review & editing. **Malgorzata Korzeniowska:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Yuyun Lu:** Writing – review & editing. **Baoru Yang:** Writing – review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

the data is included in the manuscript

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