

Research Article

Effect of Ozonation on the Properties of Dry and Moisturized Bread Wheat Grain with and without Bran

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Abstract: The effects of ozone gas on the color, pH and gelatinization properties of dry and moisturized bread wheat grain with and without bran were investigated in present study. Dry and wetted grain samples were ozonated for 2 hours at 18°C. Ozonation increased the brightness for both dry and wet grains with and without bran. Presence of high moisture caused more increase in brightness for samples without bran after ozonation. Ozone gas decreased redness of wheat grains with and without bran. Moisturizing caused the more decrease in redness for samples without bran after the ozone process. Ozonation of dry wheat grains both with and without bran resulted in yellowness decrease, while wet wheat grains both with and without bran were not affected by ozonation process. Ozone gas caused the sharp decrease in the pH value of grain samples especially in the presence of moisture. Onset and peak temperatures of ozonated wheat grains with bran increased significantly for both dry and wet samples while the enthalpy was reduced only for wet sample with bran. However, any significant change in onset temperature, peak temperature and enthalpy was not determined for both dry and moisturized wheat grains without bran after ozonation process.

Ozonlamanın Kepekli/ Kepeksiz Kuru ve Nemlendirilmiş Ekmeklik Buğday Taneleri Özellikleri Üzerine Etkileri

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Anahtar kelimeler

Kepek,
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Nemlendirme,
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Öz: Bu çalışmada, ozon gazının, kepekli ve kepeksiz kuru ve nemlendirilmiş ekmeklik buğday tanesinin renk, pH ve jelatinleşme özellikleri üzerine etkileri incelenmiştir. Kuru ve nemli tane örnekleri 18°C'de 2 saat ozonlanmıştır. Ozonlama, kepekli ve kepeksiz hem kuru hem de nemli tanelerin parlaklığını arttırmıştır. Yüksek nem oranı, kepeği olmayan numunelerde ozonlamadan sonra daha fazla parlaklık artışına neden olmuştur. Ozon gazı, kepekli ve kepeksiz buğday tanelerinin kırmızılık oranını azaltmıştır. Nemlendirme işlemi, ozonlamanın kepeği olmayan numunelerin kırmızılık oranında daha fazla azalmaya neden olmuştur. Kepekli ve kepeksiz kuru buğday tanelerinin ozonlanması sarılık oranının azalmasına neden olurken, kepekli ve kepeksiz nemli buğday taneleri ozonlama işleminden etkilenmemiştir. Ozon gazı, özellikle nem varlığında, tane örneklerinin pH değerlerinde keskin bir düşüşe neden olmuştur. Kepeğe sahip ozonlanmış buğday taneciklerinin başlangıç ve tepe sıcaklıkları hem kuru hem de nemli numuneler için önemli ölçüde artarken, entalpi sadece kepekli nemli numuneler için azalmıştır. Bununla birlikte, ozonlama işleminden sonra hem kuru hem de nemlendirilmiş buğday taneleri için başlangıç sıcaklığı, tepe sıcaklığı ve entalpi üzerinde önemli bir değişiklik tespit edilmemiştir.

1. Introduction

Ozone, O₃, is the triatomic form of oxygen. It has various applications as a powerful oxidant based on having high reactivity and penetrability, additionally its spontaneous decomposition to a nontoxic product (Khadre et al., 2001; Mahapatra et al., 2005). Ozone applications on water treatment is widespread around the world. Ozone has been used both to treat the drinking water (von Gunten, 2003a and 2003b; Chand et al., 2007; Kasprzyk-Hordern et al., 2006) and to improve wastewater treatment units, such as sedimentation, chemical or biological oxidation processes (Beltrán et al., 2001).

Ozone was regarded as a strong antimicrobial agent for food processing in Japan, France, and Australia and then, in 1997, it was approved as generally recognized as safe (GRAS) by the Food and Drug Administration (FDA) of the U.S. Nowadays, the food industry has been interested considerably in ozone use to extend the shelf-life and to provide the safety of foods (Rice et al. 1982; Graham, 1997; Kim et al., 1999; Kim et al., 2003; Çatal and İbanoğlu, 2010). On the other hand, there is a limited number of research on ozonation of food materials, especially cereals and cereal-based products. In the past studies, ozone was generally used to inactivate microorganisms or prevent their growth by washing with ozonated water and storage under ozone gas for cereal (wheat, barley, maize) grains and flours (Naito and Takahara, 2006; Allen et al., 2003; Wu et al., 2006; İbanoğlu, 2001 and 2002; Kells et al., 2001; Mendez et al., 2003). In recent years, studies about the effects of ozonation on the many properties of macromolecules (starch, protein, etc.) such as structure, physico-chemical, thermal, pasting, flow, gelatinization properties has been becoming popular (Çatal and İbanoğlu, 2012a; 2012b; 2013 and 2014, Uzun et al., 2012; Çatal, 2015).

Further research is required not only to observe the benefits and limitations of ozone use applications in cereal industry, but also to understand the changes in the properties of ozonated cereals. The purpose of present study is to investigate the effect of ozone use on the physical (moisture content and color), chemical (pH) and gelatinization properties of whole bread wheat grains together with the presence and absence of bran based on the dry and moisturized forms. The results obtained by present study will lead to better understanding of the basic changes in the cereals when ozonated.

2. Material and Methods

2.1. Wheat grain samples

Whole hard wheat grains with bran and without bran were used as raw materials. The bread wheat (*Triticum aestivum* L.) samples from Southeastern Anatolia Region were obtained from commercial miller in Gaziantep, Turkey.

2.2. Moisturizing of wheat samples

200g of hard wheat grain samples with and without bran were immersed into 400mL distilled water for 0, 1, 2, 3, 5, 6 and 7 hours at room temperature to improve the diffusion of ozone gas into grain samples. After the rough water was removed the samples, they were milled to obtain wheat flour. Moisture contents were determined by moisture analyzer (Metler Toledo, MJ33 Moisture analyzer, Switzerland). Moisturizing or wetting time was determined according to the maximum moisture content of grain sample to prevent it converting into the paste (the grain paste was not suitable for further experiments). Wetting times were determined as 5hr for bread wheat grain with bran due to difficulty in impermeability of bran and 2 hr for bread wheat grain without bran.

2.3. Ozonation of wheat samples

Ozone gas was provided by an ozone generator (OMS Model Ozone Generator, İzmir, Turkey) using the coronal-discharge method. There is a mixing part, a degasser for removing of undissolved ozone in water, a redox control (ORP) system and an integrated oxygen unit using atmospheric air in the generator. It has a maximum ozone production capacity of 60.0 g h⁻¹. Gas is directed from the generator to a glass bottle by a connection whose end was equipped with a gas disperser (Fig. 1). Both dry and wetted grain samples were ozonated in the special glass gas bottle by ozone gas for 2 hours at 18°C

temperature and moisture contents of ozonated samples were determined by moisture analyzer. An unozonated samples were used as control samples.

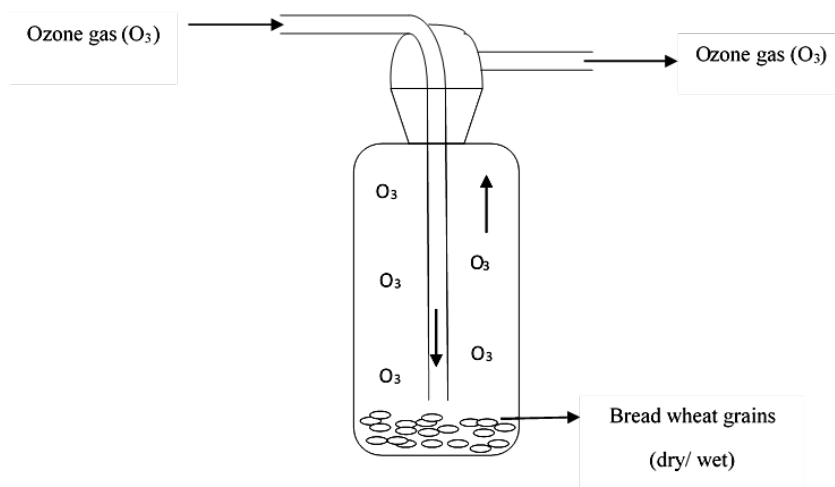


Figure 1. Schematic diagram of glass gas bottle for ozonation.

2.4. Color measurement

Color values of all control and ozonated bread wheat grains with bran and without bran were measured with a HunterLab ColorFlex (A60-1010-615 Model Colorimeter, Hunter lab, Reston VA). A white standard plate ($L_o = 93.01$, $a_o = -1.11$, $b_o = 1.30$) was used to calibrate the colorimeter. Duplicate measurements for L, a, and b were done where L is the brightness coefficient from dark (0) to bright (∞), a is the coefficient from green (-) to red (+) and b is the coefficient from blue (-) to yellow (+).

2.5. pH measurement

The pH values of control and ozonated bread wheat samples with bran and without bran were determined by a pH-meter (Hanna instruments, pH 211, Microprocessor pH-meter, Portugal). All pH analyses of starch samples were carried out in duplicate.

2.6. Thermal measurement by Differential Scanning Calorimetry (DSC)

Control and ozonated bread wheat samples with bran and without bran were analyzed using DSC (Perkin-Elmer DSC 6 equipped with a Pyris software, Perkin-Elmer Inc., Wellesley USA). 50 μ l of wheat flour-water suspension (1:9 ratio of dry sample to water) was placed into a DSC pan with a micropipette. An empty pan was used as reference. The samples were heated at a rate of 5°C min⁻¹ from 5 to 150°C using nitrogen flushing (40mL min⁻¹). The starch gelatinization characteristics (onset temperature, T_o , peak temperature, T_p and enthalpy, ΔH) were calculated by the software provided by the DSC system. Samples were analyzed in duplicate.

2.7. Statistical analysis

Statistical analysis (SPSS 13.0 software for Windows) was performed to compare the experimental results under the ozone treatment and untreated control by using a one-factor analysis of variance (ANOVA). All experimental values are at least mean of duplicate determination. In order to determine the data that are significantly different from each other, Duncan multiple range test method was applied. Trends were considered significant when means of compared parameters differed at $P \leq 0.05$ significance level.

3. Results and Discussion

3.1. Moisture content properties as preliminary study

Table 1 shows the moisture content values of bread wheat grains with and without bran. There is not a significant difference between moisture contents of control dry grain samples (5.98%) and ozonated dry grain samples with bran (5.95%) ($P>0.05$). Similar values were determined for dry grain samples (5.35%) and ozonated dry grain samples without bran (5.41%) ($P>0.05$). However, after 5 hr wetting process for grain with bran (33.42%) and 2 hr wetting process for grain without bran (34.75%) increased the moisture content significantly as an expected result ($P\leq 0.05$). After ozonation of wetted grain samples with bran (20.19%) and without bran (21.02%), moisture content decreased significantly due to moisture migration from the grain body into the air ($P\leq 0.05$). The aim of wetting process is to determine the effect of ozone gas diffusion on the properties of wheat grain samples for further experiments.

Table 1. Moisture content values of control and ozonated bread wheat samples

Bread wheat grain	with bran	without bran
Moisture content of controls (%)	5.98±0.05 ^a	5.35±0.09 ^a
Moisture content after ozonation- no wetting (%)	5.95±0.06 ^a	5.41±0.09 ^a
Moisture content after wetting (%)	33.42±0.10 ^c	34.75±0.08 ^c
Moisture content after wetting and ozonation (%)	20.19±0.06 ^b	21.02±0.07 ^b

Values followed by the different letter in the same column are significantly different ($P\leq 0.05$). Means (\pm standard deviation) are based on duplicate analyses.

3.2. Color characteristics

The measured values of control and ozonated wheat grain samples were demonstrated in Table 2. According to these data, L value, 77.60, of wheat with bran increased, while a value, 3.48, decreased significantly for both dry and wetted samples after ozonation ($P\leq 0.05$). b value, 15.57, for dry wheat grain with bran decreased after ozone gas application ($P\leq 0.05$). However, there is not any significance change for wetted wheat grain with bran after ozonation ($P>0.05$). Beside this, L value, 79.90, of dry wheat grain without bran increased significantly after ozonation ($P\leq 0.05$). On the other hand, moisturizing process for wheat grain without bran caused the increase in L value significantly after ozone gas application to sample ($P\leq 0.05$). Similarly, a value, 3.09, decreased after ozonation for dry samples without bran and more decreased in the presence of moisture for wet samples without bran ($P\leq 0.05$). b value, 23.08, for dry wheat grain without bran decreased after ozone gas application ($P\leq 0.05$). However, there is not any significance change for wetted wheat grain without bran after ozonation ($P>0.05$).

L value which is the brightness coefficient from dark to bright, was increased after ozonation for both dry and wet grains with and without bran. Beside this, presence of high moisture caused more increase in brightness for samples without bran after ozonation. a value which means the coefficient from green to red, was decreased for wheat grains with and without bran due to ozonation in present study. Moisturizing caused the more decrease in redness for samples without bran after the ozone process. b value is the coefficient from blue to yellow. Ozonation of dry wheat grains both with and without bran resulted in yellowness decrease, while wet wheat grains both with and without bran containing high moisture were not affected by ozonation process. A high value for brightness for starch are widely accepted by the consumer (Gani et al., 2010; Ikegwu et al., 2010; Thao and Noomhorm, 2011). Ozone gas or its aqueous form has the ability to decolorize some food components by oxidizing the pigments (İbanoğlu, 2002). In the present study, the color of ozonated bread wheat samples

especially moisturized ones could meet the consumer bread preference due to the higher brightness caused by ozone oxidation.

Table 2. Color and pH parameter values of control and ozonated bread wheat samples

Bread wheat grain	L	a	b	pH
Wheat with bran (control)	77.60±0.14 ^a	3.48±0.02 ^c	15.57±0.15 ^b	6.14±0.09 ^d
“Wheat with bran” ozonated	81.33±0.09 ^c	2.83±0.03 ^b	13.60±0.10 ^a	5.70±0.05 ^c
“Wheat with bran” wetted and ozonated	81.18±0.13 ^c	2.57±0.05 ^b	15.45±0.11 ^b	2.48±0.05 ^a
Wheat without bran (control)	79.90±0.08 ^b	3.09±0.03 ^c	23.08±0.014 ^d	6.36±0.08 ^d
“Wheat without bran” ozonated	82.31±0.12 ^d	2.24±0.04 ^b	19.61±0.09 ^c	3.77±0.04 ^b
“Wheat without bran” wetted and ozonated	84.08±0.13 ^c	1.30±0.02 ^a	22.02±0.013 ^d	2.26±0.05 ^a

Values followed by the different letter in the same column are significantly different ($P \leq 0.05$). Means (\pm standard deviation) are based on duplicate analyses.

3.3. pH properties

The pH values were determined for bread wheat grain samples (Table 2). It was observed that pH values of control samples with bran (6.14) and without bran (6.36) are very near neutral value. However, ozonation process caused the sharp decrease in the pH's of grain samples with bran and without bran especially in the presence of moisture (2.48 and 2.26) ($P \leq 0.05$). pH value of dry grains with bran had less decrease due to impermeability of bran surface for ozone gas diffusion into product. The pH value is a measure of the acidity or basicity of a solution that has an important effect on both growth and metabolism of microorganisms. Each microorganism has an optimum pH for its growth. The internal pH of cells is near neutrality. If the cytoplasmic pH is sufficiently reduced, growth no longer is possible and the cell eventually dies (Erkmen and Bozoğlu, 2008). A low microbial population is important for the quality of wheat. The ozonation process can eliminate contamination by bacteria and fungi during wheat flour production and can provide safer bread by reducing pH.

3.4. Thermal gelatinization properties by DSC

The values of starch gelatinization characteristics of control and ozonated wheat grain samples were shown in Table 3. It was determined that onset temperatures (60.12°C) and peak temperatures (67.89°C) of ozonated wheat grain samples with bran increased significantly for both dry (To: 61.78°C; Tp: 68.47°C) and wet samples (To: 63.02°C; Tp: 68.99°C), while the enthalpy to supply complete starch gelatinization was reduced only for wet sample with bran (ΔH : 3.9229 J g⁻¹) ($P \leq 0.05$). However, any significant change in onset temperature, peak temperature and enthalpy was not determined for both dry and wheat grains without bran after ozonation process ($P > 0.05$). Presence of bran together with ozonation caused to change in gelatinization characteristics, while absence of bran did not have any effect on the gelatinization properties.

Untreated control wheat starch thermograms were shown in Fukuoka et al.'s study (2002). The first peak for starch was observed at 55–75 °C for all samples in the moisture content ranging from 3.0 to 0.54 (g water g starch⁻¹) according to the results of that research. Besides this, transition temperatures and also enthalpy of endothermic peaks of flours (wheat, corn, rice, potato, etc.) heated in the presence of excess water (70%, w/w) were presented by another study (Liu et al., 2006). In present study, these range was confirmed for control wheat grain samples both with and without bran. Chan et al. (2011) investigated the effects of oxidation of dry powder starch by ozone gas use for 1-10 min to see the thermal property change. However, no differences were noted in gelatinization temperatures and gelatinization enthalpies of all ozone oxidized starches compared to unmodified starch. This may be due to inadequate ozonation time and/or absence of moisture. Because water holds more ozone than air and ozone needs to remain in the water long enough to disperse fully (Tiwari et al., 2010), this greatly increases the ozone penetration into the starch granule.

Table 3. Gelatinization characteristic values of control and ozonated bread wheat samples

Bread wheat grain	T _o (°C)	T _p (°C)	ΔH (j g ⁻¹)
Wheat with bran (control)	60.12±0.17 ^a	67.89±0.23 ^b	4.6169±1.09 ^b
“Wheat with bran” ozonated	61.78±0.21 ^b	68.47±0.30 ^c	4.6260±0.95 ^b
“Wheat with bran” wetted and ozonated	63.02±0.25 ^c	68.99±0.28 ^d	3.9229±0.89 ^a
Wheat without bran (control)	59.99±0.19 ^a	67.11±0.19 ^a	4.4160±1.05 ^b
“Wheat without bran” ozonated	60.09±0.25 ^a	66.99±0.21 ^a	4.4285±1.01 ^b
“Wheat without bran” wetted and ozonated	60.11±0.24 ^a	67.05±0.19 ^a	4.4954±1.13 ^b

Values followed by the different letter in the same column are significantly different ($P \leq 0.05$). Means (\pm standard deviation) are based on duplicate analyses.

4. Conclusion

In present study, ozonation increased the brightness for both dry and wet grains with and without bran, while decreasing the redness. Presence of moisture in bread wheat grains without bran caused ozonation to be more effective on those color characteristics. Ozonation of dry wheat grains both with and without bran resulted in yellowness decrease, while wet wheat grains both with and without bran were not affected. Ozone gas caused also the sharp decrease in the pH values of grain samples with bran and without bran especially moisturized ones. The onset and peak temperatures of ozonated dry and moisturized wheat grain samples with bran increased, while reducing the enthalpy just for wet grains with bran. However, any significant change in onset, peak temperatures and enthalpy was not determined for both dry and wheat grains without bran after ozonation. Presence of bran together with ozonation caused to change in gelatinization characteristics, while absence of bran did not have any effect on the gelatinization properties.

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