Short Communication

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Low Field NMR Studies of Wheat Bread Enriched with Potato Juice During Staling

Abstract: Potato juice is a by-product in the production of starch from potato tubers. However, published studies indicate that it is a source of bioactive compounds with antioxidant and anti-inflammatory effects. The use of health-promoting additives may, however, affect the quality of the fresh final product as well as the stored one. Water behavior is one of the parameters whose analysis allows for the monitoring of the shelf life of products. Therefore, the research reported in this paper was aimed at investigating the effect of replacing wheat flour with spray-dried potato juice (SDPJ) at 2.5%, 5% and 7.5% on water behavior during bread staling. ^{1}H Nuclear Magnetic Resonance (NMR) was used to analyze the impact of SDPJ on the dynamics of water in bread crumb. The NMR analyzes revealed that 7.5% addition of SDPJ resulted in an increased ratio of bound to bulk water (decreased T_1 spin-lattice time) and decreased mobility of bulk water (decreased T_{22} spin-spin time). The enriched breads also showed different dynamics of water during storage, however, in each of the analyzed variants a slight increase in T_1 was noted. It has also been shown that enrichment of bread in SDPJ accelerates the evacuation of water from the polymer network.

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1 Introduction

Potato juice, formed as one of the waste products in the potato starch production process, contains the majority of potato tuber nutrients, with the exception of fiber and starch. It consists of mineral compounds, protein, vitamins and glycoalkaloids, mainly solanine and chaconine (Barceloux 2009). With 1 ton of potatoes, up to 500 kg of potato juice can be produced, which are cumbersome to manage as waste due to the very high oxygen demand during the disposal process (Lasik et al. 2002). However, it can also be used as a substrate for the production of valuable metabolites by microbiological methods (Bzducha-Wróbel et al. 2018b, 2018a, 2015). Literature reports show that potato juice is a valuable raw material not only because of its high nutritional value, but above all due to the biological activity used in the therapy of certain diseases of the gastrointestinal tract (Kujawska et al. 2018). The biological activity of potato juice makes it an interesting addition to food production targeted at people suffering from inflammatory bowel disease (Kowalczewski et al. 2015a; Kowalczewski et al. 2015b). The enrichment of food with pro-health ingredients may, however, significantly affect the characteristics of the fresh product as well as changes during its storage.

Bread staling is a process that results in the hardening of the crumb, softening of the crust and losing the characteristic fresh taste of the product. During storage, the main ingredients of bread, i.e. starch, gluten and water, undergo significant changes. The importance of starch in the staling process has been precisely described, but evidence is also available to indicate that other factors contribute to changes in the quality of the bread during storage (Gray and Bemiller 2003). It is further assumed that water plays a fundamental role in bread staling in terms of macroscopic and molecular redistribution. The migration of water from the inside of the crumb to the skin is a macroscopic process, but changes also occur at the molecular level, where the water changes its location and status. It was found that the molecular dynamics of

water (analyzed by Nuclear Magnetic Resonance - NMR) decreases during storage (Chen et al. 1997; Curti et al. 2011). Low Field NMR is a noninvasive and nondestructive method used in analysis of the molecular properties of water in food (Baranowska 2011; Makowska et al. 2017; Piątek et al. 2013; Płowaś-Korus et al. 2018). It involves measurements of the relaxation time spin-lattice T_1 and spin-spin T_2. Both parameters characterize the molecular dynamics of water in the tested sample. Changes in their values reflect the relative changes in bulk water relative to bound water (T_1), and describe the molecular dynamics of both water fractions. Literature data suggests that changes in water behavior are connected with the texture of the product (Li et al. 2013). Therefore, the aim of the research was to analyze the impact of replacing wheat flour with spray-dried potato juice on the molecular properties of water during the staling process. The obtained results may be an important indicator of the durability of such bread because molecular changes are usually noticeable earlier than macroscopic ones, such as mold growth or a significant increase in hardness.

2 Materials and methods

2.1 Materials

Spray-dried potato juice (SDPJ) was prepared according to Kowalczewski et al. (2019b). Freshly squeezed potato juice was obtained as a by-product of potato starch production from a starch plant (WPPZ S.A., Luboń, Poland). The spray drying was performed with a pilot scale P-dryer Niro Atomizer 6.3 (Denmark) under the following conditions: air temperature at the inlet of the drying chamber was 170 °C and 95 °C at the outlet, juice flow rate was kept at 12 dm³/h. The wheat flour (type 500) was purchased from a mill GoodMills Polska sp. z o.o. (Grodzisk Wielkopolski, Poland), compressed baker's yeast from Lesaffre (Wołczyn, Poland) and salt from Kopalnia Soli 'Kłodawa' S.A. (Kłodawa, Poland).

2.2 Bread preparation

The previously described method by Kowalczewski et al. (2019a) was used for bread preparation. The reference wheat bread (denoted as R in the text) was prepared without any addition of SDPJ. The recipe for R was as follows: 500 g wheat flour, 7.5 g salt, 15 g yeast and 300 g water. In the test samples wheat flour was replaced with SDPJ in three different quantities of 2.5%, 5.0% and 7.5% with respect to the used flour weight, and were named as SDPJ2.5, SDPJ5.0, and SDPJ7.5, respectively. The dough was prepared using a straight dough method with the KitchenAid (model 5KPM5EWH, KitchenAid, USA) mixer for 10 min at a speed of 70 rpm, fermented in the fermentation chamber for 60 min (temperature 30°C, relative humidity 75%), divided into two parts (around 400 g each), hand-molded, proofed for 20 min, and baked at 230°C for 30 min (MIWE Michael Wenz GmbH, Amstein, Germany). Afterwards the obtained breads were left at room temperature for 2 h to cool down, weighed and heat sealed in in polypropylene bags and stored for 4 days at room temperature for further evaluations.

2.3 NMR relaxometry

The NMR measurements were determined according to Baranowska et al. (2018). The crumb samples of 1.5 cm³ were placed in measuring test tubes and sealed using Parafilm®. Measurements of the spin-lattice (T_1) and spin-spin (T_2) relaxation times were performed using a pulse NMR spectrometer MSL30 operating at 30 MHz (WL Electronics, Poznań, Poland). The crumbs were measured at 21.0 ± 0.5°C. The inversion-recovery (Brosio and Gianferri 2009) pulse sequence was applied for measurements of the T_1 relaxation times. Calculations of the spin-lattice relaxation time values were performed with the assistance of the CracSpin program (Jagiellonian University, Cracow, Poland) (Weglarz and Haranczyk 2000). The program for calculating relaxation parameters from experimental data uses 'spin grouping' approach. Marquardt`s method of minimization has been applied for fitting multiexponential decays. The accuracy of the relaxation parameters has been estimated with the standard deviation.

Measurements of the spin-spin (T_2) relaxation times were taken using the pulse train of the Carr-Purcell-Meiboom-Gill spin echoes ($90-\tau/2-(180)_n$) (Brosio and Gianferri 2009). The distance (τ) between 180 RF pulses amounted from 0.7 to 0.8 ms. The repetition time was 10 s. The number of spin echoes (n) amounted to 100. Five accumulation signals were employed.

The calculations were performed by using the dedicated software by application of a non-linear least-square algorithm. The accuracy of the relaxation parameters has been estimated with the standard deviation. The presence of two proton fractions was determined for all analyzed systems.

2.4 Statistical analysis

All the measurements were repeated three times, unless stated otherwise. One-way analysis of variance (ANOVA) was carried out independently for each dependent variable. The post-hoc Tukey HSD multiple comparison test was used to identify statistically homogeneous subsets α = 0.05. Statistical analysis was performed with Statistica 13 software (Dell Software Inc., USA).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

The published results showed a significant impact of SDPJ on the texture parameters of bread (Kowalczewski et al. 2019a). Application in the SDPJ recipe resulted in a significant increase in the firmness of the crumb. This paper presents changes in water dynamics in bread during storage. Table 1 presents the results of measurements of relaxation times spin-lattice T_1 and spin-spin T_2 in the analyzed bread. The presence of two components of the spin-spin T_2 relaxation time is characteristic for the analysis of such materials (Kowalczewski et al. 2019b; van Nieuwenhuijzen et al. 2010). The short component T_{21} describes the immobile state of water fractions. The mobile water fraction is described by the long component of the spin-spin relaxation time. The results obtained 2 hours after baking (after cooling down the bread) show that the substitution of flour with SDPJ limits the amount of bulk water in relations to bound water, which is manifested by smaller values of relaxation time spin-net T_1. It is worth remembering that the biopolymers present in the dough, i.e. gluten and starch, have different water-binding properties (Doona and Baik 2007). In addition, with increasing amounts of SDPJ addition decreases the amount of bulk in relation to the bound water. The reduction of the relaxation times T_{21} and T_{22} in the samples containing SDPJ, as compared to the control sample, is the effect of suppression of the molecular dynamics of water. It should be noted, however, that the amount of substitution of wheat flour with SDPJ does not significantly affect the mobility of the bound fraction. The reduction in the time value T_{21} is only related to the reduction in the amount of wheat flour in bread, which confirms the observed two-fold decrease in the value of relaxation times T_{22} for samples of dried bread as compared to the control sample. At the same time, the role of SDPJ as the binding agent of the bulk fraction molecule is confirmed by analyzing the T_{22} values for individual trials. The more flour replaced with SDPJ, the more the molecular dynamics of the bulk water fraction is inhibited. Similar effects of changes in relaxation times due to the enrichment of bread were observed in the studies of Curti et al. (2013), where the effect of the addition of the fractions on bread properties was investigated. It was shown that along with the increase in the amount of the additive the relaxation time values decreased.

Measurements of relaxation times in individual bread crumb samples indicate a significant effect of the addi-

Table 1: The NMR relaxometry measurement results

Sample	T_1 [ms]	T_{21} [ms]	T_{22} [ms]
Measurement after 2 h			
R	89.54 ± 0.97[a]	3.10 ± 0.70[a]	8.50 ± 0.25[a]
SDPJ2.5	70.03 ± 0.73[b]	1.53 ± 0.17[b]	4.92 ± 0.20[b]
SDPJ5.0	67.70 ± 1.33[c]	2.00 ± 0.49[ab]	4.69 ± 0.62[b]
SDPJ7.5	61.37 ± 0.20[d]	1.63 ± 0.71[b]	4.26 ± 0.91[b]
Measurement after 24 h			
R	90.00 ± 0.20[a]	1.23 ± 0.33[a]	7.16 ± 0.61[a]
SDPJ2.5	76.50 ± 0.30[b]	1.05 ± 0.23[ab]	4.88 ± 0.28[b]
SDPJ5.0	70.50 ± 2.20[c]	0.98 ± 0.07[b]	3.79 ± 0.30[c]
SDPJ7.5	64.00 ± 0.20[d]	1.05 ± 0.16[ab]	3.63 ± 0.80[c]
Measurement after 96 h			
R	95.20 ± 2.20[a]	1.31 ± 0.65[c]	6.21 ± 0.65[a]
SDPJ2.5	77.40 ± 1.10[b]	1.74 ± 0.91[b]	5.57 ± 0.50[b]
SDPJ5.0	72.90 ± 0.20[c]	1.89 ± 0.26[b]	5.70 ± 0.21[b]
SDPJ7.5	67.00 ± 1.90[d]	2.50 ± 0.30[a]	5.78 ± 0.18[b]

Mean ± SD values denoted by different letters differ statistically significantly (p < 0.05).

tion of SDPJ on the molecular dynamics of water during the staling process. It has been noticed that all samples are characterized by one spin-lattice time T_1, so during the entire staling process a proton exchange of both water fractions takes place very quickly. There is a slight increase in T_1 during storage of bread. This can be interpreted as the release of water molecules due to the starch retrogradation process, which is confirmed by the published data of a slight change in moisture content and water activity (Curti et al. 2013). For the crumb of bread without the addition of SDPJ, a noticeable (about 6%) increase in the T_1 value is noticed until after 4 days of storage. In the samples containing SDPJ, the highest increase in T_1 (by about 9%) is observed after the first day of storage, and the next 3 days is a change by a further 1%. In samples where the substitution of flour by SDPJ was 5% and 7.5%, an approximately 4% increase in T_1 after the first storage day was observed, and a further 4% and 5% increase in T_1 after 3 consecutive days. Thus, SDPJ significantly increases the amount of bulk water in relation to the bound in the crumb subjected to staling processes. The bulk fraction in R is characterized by a gradual limitation of the possibility of movement which is manifested by a decrease in the T_{22} value over time. In the case of samples containing SDPJ, there is a limitation of the molecular dynamics of this fraction of water after 1 day of storage. After the next 3 days, the mobility of the bulk water molecules increases and in the case of SDPJ7.5, the T_{22} components reach higher values than those indicated in the bread immediately after baking. This confirms the influence of the presence of SDPJ on the molecular properties of water in the bread crumb. The decrease in the relaxation time T22 is probably the result of retrogradation of starch (Farhat et al. 2003) and/or water redistribution in the amorphous regions of the sample (Hallberg and Chinachoti 2002; Vodovotz et al. 2002). The bound water fraction, whose molecular dynamics are described by the T_{21} component, is characterized by comparable values of these parameters for all analyzed samples. This means that the presence of SDPJ does not determine the dynamics of water molecules directly related to the biopolymer matrix.

4 Conclusion

The presented results of research on the impact of wheat flour substitution with dried potato juice, analyzed at the molecular level, showed changes determined by the presence of a health-promoting ingredient. The content of SDPJ at the level of 7.5% significantly affects the quality of

water binding in the crumb during staling. The observed changes should be interpreted as important from the point of view of bread storage quality. After 4 days, as a result of staling, in the crumb containing the SDPJ, the water from the polymer network is evacuated. The result is a greater risk associated with the possibility of molding bread. The SDPJ can be used in bread, but its large addition shortens the shelf life of bread.

Conflicts of Interest: On behalf of all authors, the corresponding author states that there is no conflict of interest.

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