Toasting Time and Cooking Formulation Affect Browning Reaction Products Development in Corn Flakes

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ABSTRACT

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During toasting, the last stage of corn flake production, Maillard reaction takes place, favored by the high temperature and low water content. The cooking formulation ingredients influence color and flavor of the final product and, therefore, consumer acceptance. However, some undesirable components are also formed. The impact of cooking formulation and toasting time on color development and on the formation of chemical markers was investigated. Samples (flakes) were equilibrated at water activity (a_w) 0.8 and toasted at 230°C. After extraction of fluorescent pigments with pronase, fluorescence, absorbance at 420 nm, and furfurals analysis was performed. Sucrose showed a synergistic interaction with malt and salt. Formulation highly affected the amount of 5-hydroxymethylfurfural and furfural formed. L^* and a^* were sensitive variables to measure overall browning reaction. These results allow for further understanding of the influence of formulation used during cooking and would help to mitigate the formation of undesirable compounds.

Commercially available corn flakes are usually produced by two different alternative processes: flaking or extrusion. This work focuses on the classical flaking method, which begins with grits mixed with water, sugar, salt, and malt extract as formulating agents, after which the grits are cooked under saturated steam. During this process, the starch is gelatinized and nonenzymatic browning takes place (Farroni and Buera 2012). Cooked grits are cooled, flaked, and toasted in a stream of air at high temperature (approximately 230°C) for a short time (a few minutes) to obtain the final product. During toasting, the Maillard reaction further develops under conditions at which dehydration reactions occur.

At high temperatures, sugars decompose into furfural (F) compounds by two possible pathways, both involving a first step of sucrose hydrolysis: caramelization, in which the reducing carbohydrates directly suffer 1–2 enolization, dehydration, and cyclization reactions; and the Maillard reaction, in which the Amadori products (formed by reaction of the amino group of free amino acids or proteins with reducing carbohydrates) are submitted to isomerization and subsequent dehydration of the sugar moiety (Ait-Ameur et al. 2006). The intermediate steps of the Maillard reaction include the formation of unsaturated and saturated compounds involved in the formation of pigments. Some of these pigments may act as crosslinking agents between protein chains, either decreasing food nutritional value or impairing its organoleptic properties (Agudelo-Laverde et al. 2011). Furthermore, some of the possible resulting compounds such as acrylamide are considered potentially mutagenic (Rufián-Henares et al. 2006).

Maillard fluorescent products have been studied in model systems as potential indicators of essential amino acid damage (Farroni and Buera 2012).

The role of F as an indicator of heat treatment and a cooking marker was deeply studied (Ramírez-Jimenez et al. 2000; Ait-Ameur et al. 2006). 5-Hydroxymethylfurfural (HMF) is a decomposition product of hexoses, especially when the pH is low (Xu et al. 2003), whereas F and 5-methylfurfural (5MF) are derived mainly from pentoses (Ledl and Sevrin 1978).

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There is no previous work regarding HMF formation, advance of the Maillard reaction during the toasting of cornflakes, and the effect of different cooking formulations or ingredient interactions. Thus, the aim of this work was to study the progress of the browning reactions in the toasting stage of cornflake production by tracking HMF, F, and 5MF, CIELAB color, absorbance at 420 nm (Abs_{420}), and fluorescence as a function of formulation ingredients and toasting time.

MATERIALS AND METHODS

Sample Preparation. Proximal composition of corn grits in this study was as follows: carbohydrates, 87 ± 1%; proteins, 8.0 ± 0.3%; lipids, 0.90 ± 0.05%; humidity, 13.0 ± 0.1%; and ash, 0.20 ± 0.02% dry basis (db). Protein value was obtained by the Kjeldhal method (method 992.23) (AOAC 2003), with a nitrogen-to-protein conversion factor of 6.25. Lipids value was obtained by Soxhlet extraction (method 945.16) (AOAC 2003). Ash was measured following method 923.03 (AOAC 2003), humidity by a gravimetric method (method 925.09) (AOAC 2003), and starch by difference. Corn grits were obtained from a local factory and stored in a freezer until used. The same lot of grits was used for the entire study. Grits were processed by simulating the industrial processing conditions.

The grits were steam cooked for 2.5 h, employing six different formulations with salt, malt extract, and sucrose (Table I). Cooking formulations were selected to analyze the effect of the ingredients separately and together. Formulation A was described by Fast (2000) as a typical commercial formula, and formulation B was provided by a local manufacturing company. To analyze the effect of each ingredient, single-component formulations were prepared, maintaining the proportions used in formulation A. For each of the formulations, 15 g of raw grits was employed and incorporated into a solution with the ingredients listed in Table I. After steam cooking in a pressure cooker pot, the grits were cooled at room temperature for 1 h and flaked with a semi-industrial counter-rotating hand roller (Máquinas RD model S-300-M, Buenos Aires, Argentina). The rollers had a 6 cm external diameter and were 30 cm long, with a gap of 2 mm between them.

To perform the toasting experiments under specified conditions for all samples, the flaked corn grits were freeze dried and equilibrated in an atmosphere of controlled humidity at water activity (a_w) 0.8 for three weeks, which corresponds to a water content close to 20.0% (db). This water content is close to the value found in industrial flaked grits just before the toasting step (Farroni and Buera 2014). The selected a_w to perform the toasting process was chosen taking into account that, in amylaceous foods, the maximum rate of browning occurs below and close to a_w 0.84 (Acevedo et al. 2008b) and can reflect the changes more sensitively. Once equilibrated,

samples were toasted in a convective oven at 230°C under forced air flow. Three toasting times were studied: 1.5, 2, and 2.5 min.

Experimental Design. Experimental design consisted of six formulations, three toasting times, and a single toasting temperature and a_w. A repeated-measures design was used, in which samples were toasted from zero to the specified time. All extraction procedures for analytical purposes were made in duplicate or triplicate, as described in each section.

Chemicals. HMF, F, and 5MF were analytical standards from Sigma-Aldrich (Saint Louis, MO, U.S.A.). Furosine was from Neosystem Laboratories (Strasbourg, France). Pronase E, heptane sulphonate, and quinine sulfate were from Sigma-Aldrich. NaCl, HCl, acetonitrile, formic acid, and sucrose were from Biopack (Buenos Aires, Argentina). Corn grits and malt syrup were provided by a local breakfast cereal manufacturer (Tres Arroyos, S.A., Buenos Aires, Argentina). The commercial malt syrup used consisted of a mixture of sugars and less than 10% protein, with no diastatic activity because it was inactivated in the first stage of cooking at 121°C.

Fluorescence and Brown Pigments. Browning and fluorescence development as a function of toasting time and cooking formulation were evaluated. Total fluorescent compounds extractable in aqueous media were quantified after sample hydrolysis with pronase E, according to the method of Delgado-Andrade et al. (2008), employing 0.1M borate-buffered saline at pH 8.2. Pronase E activity was of 4 U/mg of sample, where 1 U/mg equals 1 U able to hydrolize casein, producing an equivalent absorbance to tyrosine at 1.0 µmol (181 µg)/min at pH 7.5 and 37°C, as measured by the Folin–Ciocalteu method.

Fluorescence intensity, with excitation at 340 nm, was measured at 504 nm, at which the maximum value of the emission spectrum was observed. An Ocean Optics model USB 2000 spectrofluorometer (Ocean Optics, Dunedin, FL, U.S.A.) was used. The samples employed for the determination of fluorescence were first measured at 340 nm and diluted if necessary with 0.25M phosphate buffer at pH 7, taking as general criteria that the absorbance values should be lower than 0.1 to avoid the inner filter effect. Quantification of fluorescent compounds was made on the basis of quinine emission equivalents (μg_Q/mg) in db. A calibration curve was constructed with four concentrations of quinine sulfate, in duplicate, with a concentration range of 0.05–1.00 µg/mL, as described by Matiacevich and Buera (2006). The obtained R^2 was 0.9980.

The development of extractable brown pigments was followed by measuring absorbance units at 420 nm in a UV-Vis spectrophotometer (V630, Jasco Corporation, Tokyo, Japan). This was also performed after the hydrolysis with pronase. Absorbance values were corrected by dilution and normalized to 125 mg of dry sample weight (Abs_{420}).

Duplicate extraction and duplicate assays of each extract were run. The average values are listed.

F Content. HMF, F, and 5MF were quantified in hydrolyzed samples by reverse-phase HPLC in a modification of the procedure proposed by Ait-Ameur et al. (2006). An Alliance HPLC system equipped with a Waters 2995 diode array detector was used (Waters, Milford, MA, U.S.A.). Samples were separated in a Waters X-Bridge C_{18} column, 2.1 × 100 mm and 3.5 µm particle diameter, operating at 25°C. The mobile phase consisted of 5% acetonitrile at 0.1 mL/min. Sample (10 µL) was injected, and the absorbance was monitored at 284 nm. Retention times were 7.4 min for HMF, 8.8 min for F, and 15.3 min for 5MF. Calibration curves were constructed for each analyte with the external standard method by measuring five points in duplicate, in the range of 0.1–2.5 ppm diluted in the mobile phase (R^2 = 0.9999). The quantification limit was calculated by the signal-to-noise relation and was less than 0.05 ppm for all compounds; the relative standard deviation was 3%. Average recovery was 85%, which is in the acceptable range for most of the values found in this work, according to AOAC guidelines (AOAC 2002). The three standards used were from Sigma-Aldrich. Duplicate extraction of the same sample was performed, duplicate assays of each extract were run, and the average values were expressed in milligrams per kilogram of dry sample (ppm db).

Furosine Determination by HPLC. The method used by Delgado-Andrade et al. (2007) was followed. Ground sample (30 mg) was hydrolyzed with 4 mL of 7.95M HCl at 110°C for 23 h in a Pyrex test tube with polytetrafluoroethylene-faced septa. Hydrolysis tubes were sealed under nitrogen. The hydrolysates were cooled at room temperature and subsequently centrifuged at 14,000 × g for 10 min. A 0.5 mL portion of the supernatant was applied to a Sep-pak C18 cartridge (Millipore, Billerica, MA, U.S.A.) prewetted with 5 mL of methanol and 10 mL of deionized water, and was then eluted with 3 mL of 3M HCl. Solvent was evaporated in rotary evaporator at 35°C, and the sample was resuspended in 1 mL of 5% acetonitrile. A similar Alliance HPLC system with an Extrasyl-ODS2 analytical column (25 × 0.40 cm, 5 µm particle size) (Tecknokroma, Barcelona, Spain) was used at 32°C, isocratically eluted at a 1.0 mL/min flow rate. The mobile phase consisted of 5mM sodium heptane sulphonate containing 20% acetonitrile and 0.2% formic acid. The injection volume was 20 µL and detection set at 280 nm. Furosine was quantified by the external standard method. The calibration curve was built in the range of 2.6–39 mg/L, in duplicate (R^2 = 0.9988).

Water Content. To express the results on a dry matter basis, water content of the studied samples was determined gravimetrically. Samples were ground in a mill, and aliquots of approximately 500 mg were dried at 130°C in 2 cm diameter aluminum crucibles for 1 h (method 14.003) (AOAC 1980). Measurements were performed in triplicate, and the average of results was employed to calculate dry matter.

Color Measurement. Color changes during toasting were determined by image analysis under standardized conditions. A computer vision system was employed, consisting of a standard gray box (luminance 50, Munsell scale). The interior of the box had a D65 illumination system located in the upper part designed to simulate daylight (Lawless and Heymann 1998). Images were taken with a digital camera (EOS 40D, Canon, Melville, NY, U.S.A.) located at an angle of 45° with the sample plane and at a distance of 60 cm. Image acquisition was performed with the remote capture EOS utility (Canon). The camera settings consisted of shutter speed 1/8 s (no zoom, no flash), macro focus mode, relative aperture (f) = 6.3, and ISO 100. The images were obtained with a resolution of 3,888 × 2,592 pixels and saved in JPEG format. The photographs obtained were analyzed with Adobe PhotoShopCS4 software, and color parameters were expressed in CIELAB space (L^*, a^*, and b^*) according to the procedure described by Yam and Papadakis (2004). PhotoShop software allowed the precise selection of the sample area for color quantification, avoiding background and shadowed zones. Samples were placed in plastic capsules 1.5 cm in height, at which the system behaves as opaque. Three photos were taken of each sample, rotating 90° between each, and results were averaged.

Statistical Analysis. Mathematical modeling of the kinetic data was done with GraphPad software. Split-plot analysis of variance was performed with InfoStat software (version 2012, FCA, Universidad

TABLE I
Systems Composition: Mass of Each Ingredient Mixed with 15 g of Grits for Steam Cooking Formulations

Ingredient	Control	Salt	Malt	Sucrose	Commercial Formulation A	Commercial Formulation B
Water (g)	9	9	9	9	9	6
NaCl (g)	–	0.33	–	–	0.33	0.01
Malt (g)	–	–	0.33	–	0.33	0.001
Sucrose (g)	–	–	–	1.23	1.23	1.23

Nacional de Córdoba, Argentina). A post hoc Tukey's test was used to evaluate for significant differences, with $P < 0.05$.

RESULTS AND DISCUSSION

Furfurals Development. The values of HMF concentration obtained for all samples at different toasting times are shown in Table II. HMF content of the cooked samples was approximately 10 ppm for all formulations before toasting. The toasting process produced a significant increase in HMF content for A and B formulations at 1.5 and 2 min. At the 2.5 min toasting time, only A formulation showed a significant increase in HMF. Interaction between the formulation and the toasting time was found to be statistically significant. In extruded-corn breakfast cereals, HMF values of approximately 45 ppm db were reported by Rufián-Henares et al. (2006). These values are comparable with those found in the present work for formulations prepared with only salt, malt, or sucrose and up to 1.5 min of toasting.

When sucrose was added to the formulation, a tendency of increasing HMF values could be seen in comparison with control or salt- and malt-containing systems that cannot be confirmed statistically. It is interesting to note that a difference of 30 s in the first toasting interval produced a large increase in HMF levels, indicating that this stage is critical and must be carefully controlled.

The ingredients used did not show a significant effect on HMF formation when added individually; however, after 2 min of toasting, systems A and B containing the three ingredients developed the highest HMF levels. These data indicate that sucrose, malt, and salt had a synergistic effect.

HMF concentrations increased up to approximately 2,500 ppm in formulations A and B after 2.5 min of toasting. These values are similar to those found by Ait-Ameur et al. (2006) during model cookie baking at temperatures over 250°C, at a_w values close to zero. As drying occurred during cooking, Ait-Ameur et al. (2006) detected HMF formation when a_w values decreased to less than 0.4. It is known that a_w is a fundamental parameter in HMF production (Kroh 1994). In this a_w range, the formation of 1 mol of HMF from fructose or glucose promotes the release of 3 mol of water; thus, water, being a reaction product, acts as an inhibitor (Ait-Ameur et al. 2006). The effect of salt on increasing HMF concentration in baked food was already described (Van Der Fels-Klerx et al. 2014; Mesíaset al. 2015). The mechanism underlying this effect is an object of discussion. Addition of salts can retain water in low-moisture systems, thus reducing the inhibition byproducts in dehydration reactions (Acevedo et al. 2008a). Although the initial a_w of the samples studied in the present work was quite high (0.8), flakes are thin and offer a large surface exposed at high temperatures. Thus, the a_w decreased quickly, down to final values of 0.4–0.5 during toasting. It can be seen that the main water loss occurred in the first 1.5 min (Table II). At similar a_w values, high HMF formation was reported for model cookies (Ait-Ameur et al. 2006). Two mechanisms have been proposed for the formation of HMF from sucrose, one of them via a Maillard reaction pathway starting from glucose or fructose and amino acids through several steps (Van Der Fels-Klerx et al. 2014) and the other with sucrose degrading into glucose and a reactive fructofuranosyl cation that can be effectively converted directly into HMF (Locas and Yaylayan 2008). Regarding F, only samples with added sugar had values greater than the quantification limit at 1.5 min toasting time, and the control, salt, and malt formulations showed values less than 0.05 ppm. For 2.0 and 2.5 min toasting times, no statistical differences were found among control or salt-, sucrose-, and malt-containing samples (0.65–27 ppm). As with HMF, A and B formulations presented F values significantly higher than the rest of the systems, showing a range of 99–131 ppm, thus confirming the synergistic effect of ingredients in F formation.

Petisca et al. (2014) studied the occurrence of HMF and F in baked bread and cookies. It is interesting to note that a similar order of magnitude difference between both compounds was usually found in samples with low concentrations of HMF, and sometimes even F concentration exceeded HMF. This behavior was also observed in the model samples of the present work. Nevertheless, as soon as HMF concentration rose to greater than 20 ppm, the concentration difference between both compounds increased drastically. This could be related to the different reaction kinetics but also to the difference in molecular volatility between them. It has been stated that one of the related strategies to remove F from food systems is by heating it in open vessels (Anese and Suman 2013), thus taking advantage of their characteristic volatility.

5MF was formed at low concentrations (1.5–3 ppm) in all systems. The maximum 5MF concentration values were two orders of magnitude lower than those corresponding to the maximum F values and three orders lower than the maximum HMF values. No apparent relation could be observed between the 5MF values with either the toasting times or the cooking formulations, and no statistical differences were observed between samples.

HMF was the most representative compound of the studied F, showing the highest concentrations. 5MF was detected in all samples,

TABLE II
Furfurals and Furosine Values for the Six Different Cooking Formulations Toasted at Three Toasting Times

Time, Formulation	Humidity (% wb)	HMF (ppm dm)	Furfural (ppm dm)	5MF (ppm dm)	Furosine (μg per 100 g dm)
1.5 min					
Control	9.6 ± 0.4g	14 ± 3a	<0.02a	2.0 ± 0.3	9 ± 5ab
NaCl	8.4 ± 0.4defg	8.7 ± 0.3a	<0.02a	1.8 ± 0.1	8 ± 2ab
Malt	7.7 ± 0.2cde	20 ± 2a	<0.02a	2.6 ± 0.2	6.9 ± 0.4ab
Sucrose	6.6 ± 0.5abc	53.9 ± 0.9a	7.1 ± 0.1a	2.47 ± 0.01	11 ± 2b
A	8.0 ± 0.1cdef	396 ± 13a	27 ± 1a	1.8 ± 0.3	6 ± 4ab
B	7.3 ± 0.6bcde	154 ± 16a	10 ± 8a	1.98 ± 0.09	2.3 ± 0.5a
2 min					
Control	8.6 ± 0.4efg	11 ± 4a	0.7 ± 0.6a	3.2 ± 0.2	5 ± 1ab
NaCl	9.4 ± 0.6fg	22 ± 3a	1.7 ± 0.3a	2.8 ± 0.5	3.6 ± 0.9ab
Malt	8.3 ± 0.2defg	26 ± 7a	2.83 ± 1.17a	2.5 ± 0.1	1.6 ± 0.4a
Sucrose	6.9 ± 0.6abcd	137 ± 22a	16 ± 5a	2.1 ± 0.4	3.9 ± 0.2ab
A	6.5 ± 0.2abc	1,797 ± 71b	99 ± 7b	1.5 ± 0.4	3.2 ± 0.3a
B	7.0 ± 0.4bcd	2,336 ± 72c	131 ± 21b	2.4 ± 0.2	2.1 ± 0.4a
2.5 min					
Control	8.4 ± 0.3defg	15 ± 1a	1.2 ± 0.3a	2.55 ± 0.04	2.6 ± 0.3a
NaCl	7.8 ± 0.1cde	42 ± 23a	4 ± 2a	2.4 ± 0.4	3.2 ± 0.6a
Malt	7.5 ± 0.3cde	72 ± 5a	10 ± 7a	2.0 ± 0.3	2.35 ± 0.07a
Sucrose	5.9 ± 0.6ab	114 ± 9a	14 ± 1a	2.3 ± 0.2	2.8 ± 0.3a
A	5.5 ± 0.6a	2,639 ± 186c	125 ± 58b	1.7 ± 0.6	6.1 ± 0.6ab
B	7.4 ± 0.2bcde	2,398 ± 460c	131 ± 5b	1.9 ± 0.7	4.4 ± 2.1ab

[z] Abbreviations: wb = wet basis; HMF = 5-hydroxymethylfurfural; dm = dry matter; and 5MF = 5-methylfurfural. Different letters refer to statistically significant differences within the same variable for $\alpha = 0.05$. 5MF values did not show significant differences between them.

and the F variation was statistically significant and quantified in samples A and B at 2 and 2.5 min toasting times; however, the difference between samples was not significant at lower toasting times for the formulations having a single ingredient and water.

Furosine Production. Furosine as a specific early Maillard reaction marker did not show significant changes during toasting; also, the interaction between toasting time and cooking formulation was not significant. The control sample showed a concentration of 8.5 µg/100 g. The addition of other ingredients did not promote major differences in furosine content at this stage. Complex formulations A and B surprisingly showed the lowest quantities of furosine (6.1 and 2.3 µg/100 g, respectively) and an amount of HMF over 150 ppm.

Our results suggest that, during toasting, furosine as an early Maillard reaction marker is not suffering major changes. A more detailed study of the Maillard reaction could examine other advance reaction products, even though it has been previously reported that, during the industrial processing of flakes, HMF levels increased drastically in the toasting process, whereas other markers such as carboximethyllisine (CML) did not show significant differences at this stage, so that the amount of CML was not changed after the toasting of corn flakes (Farroni and Buera 2012).

Color Changes. The chromatic variables L^* (luminosity) and a^* (redness) presented significant differences ($P < 0.01$) among the different formulations and toasting times. Interaction between formulation and toasting time was also significant. Changes in the chromatic coordinate b^* (yellowness) were less pronounced. The darkening of samples was represented by plotting the difference in luminosity before and after the toasting process ($L_0^* - L^*$) versus toasting time (Fig. 1A). Salt and malt formulations showed significant darkening after 2.5 min toasting, whereas sucrose, A, and B forumlations showed significant darkening after 1.5 min. Samples containing all ingredients (A and B) showed the most important darkening at 2.5 min. The a^* values increased significantly with the toasting time and also were highly dependent on the formulations, following a similar tendency as that found for $L_0^* - L^*$ (Fig. 1B). For the first 1.5 min, b^* values were in a range of 38.2–42.8 and did not show differences between formulations. After 2.0 and 2.5 min of toasting, the b^* values were 37–45 and still did not show significant differences between samples, except for two values at 2.5 min that were significantly lower: A (23.7) and B (30.1). An interaction between time and formulations was also observed, but no apparent relationship between time–formulation and samples could be extracted.

The CIELAB color coordinates ($L_0^* - L^*$ and a^*) increased linearly with the toasting time, indicating a zero-order reaction kinetics. In general, it was possible to visually observe that, for the formulations containing all ingredients, toasting times higher than 1.5 min promoted browning, generating a dark color that could be unacceptable to a consumer. This could be related also to the high amount of HMF detected in these samples. A significant (negative) correlation between L^* and HMF was previously reported by Kowalski et al. (2013).

Fluorescence and Browning. The obtained results of brown pigments $\ln(Abs_{420})$ and fluorescence (μg_Q/mg) for the pronase-treated samples at the different toasting times are shown in Figure 2A and B, respectively. The initial absorbance of samples before toasting was less than 0.1 and was not significantly different between sample systems. When absorbance data were analyzed statistically, interaction between time and formulation was significant. Although at 1.5 min of toasting the obtained $\ln(Abs_{420})$ values were not statistically different among samples, at 2 and 2.5 min of toasting, the ln

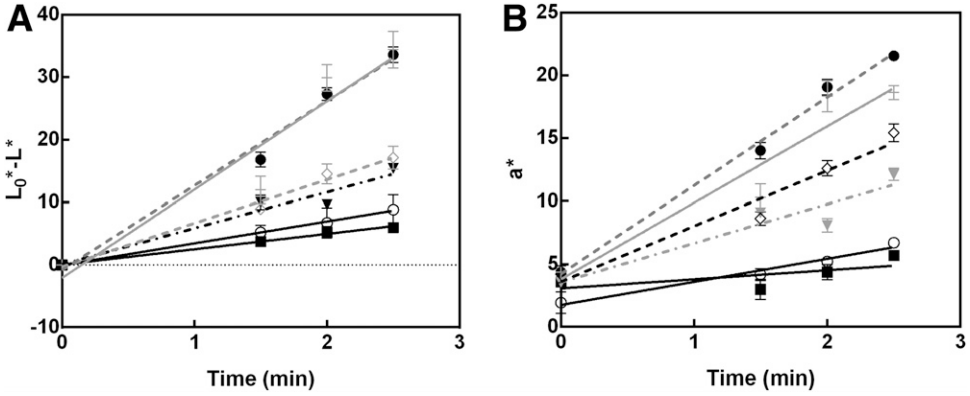

Fig. 1. A, $L_0^* - L^*$ and **B,** a^* as a function of time. Curves for the different formulations at times 1.5, 2, and 2.5 min. Symbols for each formulation: ■ = control; ○ = salt; ▼ = malt; ◇ = sucrose; ● = A; and + = B. Lines represent the predicted curves (best fit model) for the different formulations. Error bars correspond to the standard deviation.

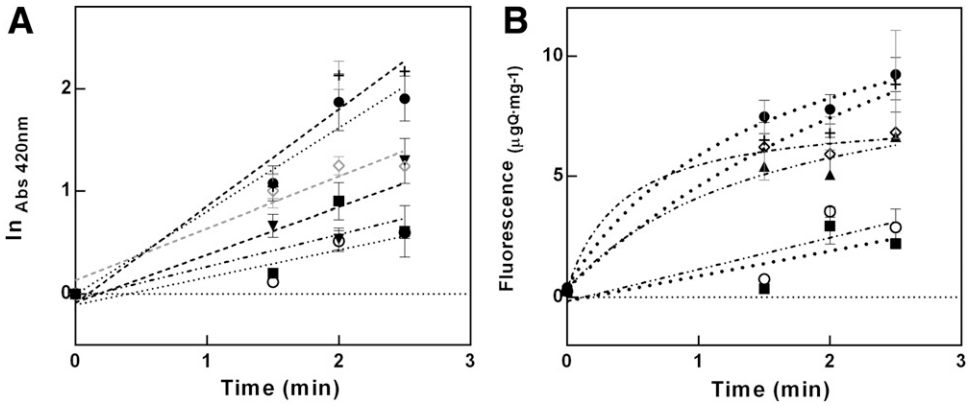

Fig. 2. A, Absorbance at 420 nm (ln Abs_{420}) and **B,** fluorescence (μg_Q/mg) for the different toasting times (1.5, 2, and 2.5 min). Symbols are the mean values for each formulation: ■ = control; ○ = salt; ▼ = malt; ◇ = sucrose; ● = A; and + = B. Error bars correspond to the standard deviation. Connecting lines present the best mathematical fit.

(Abs_{420}) values for formulations A and B were significantly higher compared with the rest of samples, except for malt at 2.5 min.

Before toasting, fluorescence was below the limit of quantification for all six flaked samples. After, it showed an initial increase with toasting time at 1.5 min. It increased linearly with toasting time for control and salt formulations. Malt, sucrose, A, and B formulations showed a rapid initial increase and then tended to reach a plateau. This behavior is expected because of their role as reaction intermediates (Morales et al. 1996) and has already been described by Patton and Chism (1951), who stated that fluorescence formation showed an induction period followed by a period of increasing concentration until a maximum was reached.

We have not observed any lag period in our systems, in concordance with the observations of Morales et al. (1996). The observation may be a result of the high-temperature conditions used in our experiment, as described also by these authors.

The interaction between time and formulation was not significant. The effect of time showed significant differences ($P < 0.05$) between the average value obtained at 1.5 min and the higher value obtained at 2.5 min. Also, individual formulations showed significant differences between them. Control and salt systems showed the lowest average values, statistically different from the average values found for the other formulations, with $P < 0.05$.

Overall, when comparing formulations A and B, no significant differences in the intermediate concentration was detected, even though B contained approximately 10 times less salt and 300 times less malt than A. Only a slight difference was observed between both systems in the color coordinate a^*, but it was attributable to the intrinsic color of malt because it was also detected at the initial time. It can be concluded that the synergistic effect of malt and salt combined with sucrose is evident even at low salt or malt concentrations, because its variation was similar in B and A systems. At the same time, sucrose individually showed a significantly lower development of browning than A and B.

CONCLUSIONS

The combined ingredients (sucrose + salt + malt) had a synergistic effect. The individual addition of small amounts of salt, malt, or sucrose did not accelerate the browning process, making this synergistic effect more important than the difference in the amounts added. Therefore, the results obtained allow us to better understand the influence of the formulation used during cooking and the effect of the toasting time in browning intermediate production. This may help to select conditions to mitigate the loss of nutrients and the generation of undesirable components.

Although not specific, during toasting of flaked corn grits, the CIELAB coordinates luminosity expressed as $L_0^* - L^*$ and redness expressed as a^* were able to promptly evaluate the degree of browning reaction showing a zero-order rate constant.

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