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The complex dependence of non-enzymatic browning development on processing conditions in maize snacks

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ABSTRACT

The complex dependence of non-enzymatic browning development on processing conditions was analyzed in the production of maize snacks. The influence of the amount of water added to maize flour, toasting time, and toasting temperature on final water contents, HMF formation and CIELAB color parameters was evaluated by Response Surface Methodology. While L^* values decreased continuously with increasing toasting temperature, the variables a^* and b^* showed maximum values at intermediate studied ranges of temperature and water contents, which is related to the complex interactions of the variables water content and temperature. The formation of HMF, as a marker of non-enzymatic browning reactions, was favored by low water contents and its concentration correlated with lower L^* and b^* but higher a^* values. The optimum levels of toasting time, toasting temperature, and water addition for minimizing HMF concentration at which the snacks presented adequate color characteristics were determined. Finally, correlations between L^*, b^* and HMF were mathematically established to predict heat damage using these fast and non-destructive indicators to assure adequate processing and storage conditions.

1. Introduction

Cereal-based products are the favorite type of snacks due to their satisfying flavor and textural properties, obtained at low costs (Gümüşay, Şeker & Sadıkoğlu (2019) ; Gupta & Bhattacharya, 2017; Rolandelli et al., 2020). Maize represents the main ingredient for the development of these foodstuffs (Cueto et al., 2015; Rolandelli et al., 2020, 2021) since it provides an excellent matrix for generating varied products with desired sensory properties. By using maize grits as a raw ingredient and through few steps of cooking, flaking, and toasting, snacks with adequate mechanical and physicochemical properties can be obtained (Cueto, Farroni, Schöenlechner, Schleining, & Buera, 2017; Cueto, Pérez Burillo, Rufián-Henares, Farroni, & Buera, 2017; Mesías, Delgado-Andrade, & Morales, 2019). Besides, it is known that there is a strong relationship between composition, processing, and final characteristics of snacks (Gupta & Bhattacharya, 2017; Nguyen, van der Fels-Klerx, & van Boekel, 2017; Rolandelli et al., 2020, 2021).

During cooking and toasting steps, flavor-related compounds and some degree of browning are developed through non-enzymatic browning reactions, which define the sensory acceptance of maize snacks (Delgado-Andrade, 2014; Gupta & Bhattacharya, 2017; Morales, Mesías, & Delgado-Andrade, 2020). Considering maize grits

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composition, the main chemical transformations that can occur during non-enzymatic browning involve both Maillard and caramelization reactions (Gómez-Narváez, Pérez-Martínez, & Contreras-Calderón, 2019). The Maillard reaction involves a complex sequence of reactions, with a first step in which an active carbonyl group (such as that of a reducing sugar) conjugates with an amino group (typically from proteins or amino acids). Caramelization is the direct conversion of reducing sugars by 1,2-enolization, dehydration, and cycling reactions (Nguyen, Van der Fels-Klerx, Peters, & Van Boekel, 2016). The common reactants in both reactions are dextrins and reducing sugars, which may be formed by starch hydrolysis during the above-mentioned process steps. However, according to the processing conditions employed, several potentially harmful products could also be formed. Compounds such as acrylamide, 5-hydroxymehtyl-2-furfural (HMF) and furans are associated to potential negative effects on consumers' health (Ghazouani et al., 2021; Gómez-Narváez et al., 2019; Mesías, Delgado-Andrade 2019, Mesías, Sáez-Escudero, Morales., & Delgado-Andrade, 2019; Mesías et al, 2019, Mesías, Sáez-Escudero, Morales., & Delgado-Andrade et al 2019, ; Nguyen et al., 2017). Hence, it is necessary to establish adequate processing conditions to obtain products with desired final characteristics but reducing the formation of harmful compounds to the minimum.

HMF may be formed through caramelization or by reaction of carbonyl groups with amino acids through the 1,2-enolization route of the Maillard reaction. On the other side, acrylamide is formed through the Maillard reaction, requiring free asparagine and carbonyl compounds (Jozinović et al., 2019; Morales et al., 2020), which are not prevailing components of maize flour. Even more diversified are the routes for furans formation, and they may involve many types of reactants (polyunsaturated fatty acids, carotenoids, sugars, amino acids, ascorbic acid) through oxidative or Maillard reactions. However, in only-cereal-based foods (with no added sugar), such as the discussed in present work, carbohydrates are the main precursors that lead to furans development, and relatively low levels of residual furans were detected in this kind of products (Kettlitz et al., 2019).

Due to the complexity of non-enzymatic browning reactions and to the high variety of products generated, suitable indicators of heat damage are necessary, that can be measured by practical and non-destructive means in order to define appropriate processing and storage conditions to maintain products quality. The quantification of acrylamide in foods is a challenge due to its high reactivity, low volatility, and high polarity which cause interferences due to interactions with the food matrix. However, a positive and strong correlation between acrylamide and HMF has been reported, independent of the type of cereal and of type of processing procedure (Jozinović et al., 2019; Morales et al., 2020). Thus, HMF is one of the most important intermediates, considered a heat-induced chemical early marker of the extent of thermal processing, since it is formed in the first reaction steps (Morales et al., 2020). Moreover, based on the relationship between product color development with the processing conditions, it is hypothesized that the CIELAB chromatic attributes may help to optimize the process parameters (Farroni, Matiacevich, Guerrero, Alzamora, & Buera, (2008) ; Gómez-Narváez et al., 2019; Cueto, Farroni, et al., 2017; Cueto, Pérez Burillo, et al., 2017; Farroni & Buera, 2012; Morales et al., 2020). Therefore, the aim of this work was to define a combination of the processing variables water addition, toasting time, and toasting temperature to produce maize snacks with the minimum HMF formation, adequate water contents and color parameters. As a second purpose, the relationship between HMF amount and the chromatic reflectance variables in the CIELAB color space was analyzed in order to challenge their use as rapid, non-destructive and accurate indicators of heat damage in these products.

2. Materials and methods

2.1. Materials and reagents

Coarsely-ground, degerminated and dehulled orange Flint maize grits (*Zea mays* L., cv. Prisma) were provided by a local company (Buenos Aires, Argentina) and stored at −18 °C until used. 5-hydrxy-methyl-2-furfural (HMF), acetonitrile (ACN) and trichloroacetic acid (TCA) were purchased from Sigma Aldrich (Saint Louis, MO).

2.2. Maize snacks preparation

Maize grits (10.0%, water content on dry basis (d.b.)) were milled using a Butt mill (Decalab S.R.L., Buenos Aires, Argentina) and meshed sieved through a No. 14 sieve to obtain maize flour of about 1.41 mm particle size. Snacks were elaborated using processing conditions close to those employed by the industry, following the methodology described by Cueto, Pérez Burillo, et al. (2017), with some modifications. Briefly, 15 g of maize flour were mixed with variable amounts of water, according to the experimental design (Section 2.3) in Petri dishes. Samples were steam-cooked for 1 h at 121 °C, 2068 hPa (30 psi), then placed over aluminum foil and left to cool in a temperature-controlled laboratory room set at 24 °C. Cooled samples were flaked using a semi-industrial counter rotating hand (RD, Buenos Aires, Argentina), with a 2 mm gap separation between rollers. Finally, flaked samples were toasted in a convective oven (A.E.W. Imperial Works, United Kingdom) under forced air flow at varying temperatures in the range from 200 to 270 °C, and times between 7 and 12 min, according to the experimental design (Section 2.3). The same batch of maize grits was used for the entire study.

2.3. Experimental design

Considering the several processing variables involved and their complex effects on the product properties, Response Surface Methodology (RSM) represents a valuable tool for defining operative parameters that lead to optimum elaboration processes conditions and final product characteristics (Favre et al., 2020; Gümüşay et al., 2019).

The different processing conditions for the elaboration of maize snacks were analyzed through a Box-Behnken design (BBD). The independent variables analyzed (X_i) with their respective levels were: water addition to 15 g of maize flour (6–12 g), toasting time (7–12 min) and toasting temperature (200–270 °C). These values range were defined according to previous tests that considered complete cooking (starch gelatinization), adequate snacks color (no over-toasting or under-toasting), and overall visual aspect of the products (Section 2.7). Moreover, the selected levels were in the range of the process variables commonly used in industrial or domestic practices (Giovanelli & Cappa, 2021; Gökmen, Çetinkaya Açar, Köksel & Acar, (2007)). The dependent variables (Y_i) or responses evaluated in the BBD were: final water content (%, d.b.), CIELAB space color parameters (L^*, a^* and b^*) and 5-hydroxymethyl-2-furfural (HMF) content (ppm). The variables codification and different combinations of the BBD are shown in Table 1.

To calculate the predicted responses a second order polynomial model was used:

$$Y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} b_{ij} X_i X_j \tag{1}$$

Where Y is the dependent variable or response value, b_0 is the offset term, b_i, b_{ii} and b_{ij} are the linear, squared and interaction effects, respectively, and X_i and X_j are the independent variables.

The experimental conditions of the dependent variables were evaluated through analysis of variance (ANOVA), regression analysis and RSM figures plotting. All results, plots and coefficients were analyzed using the Design-Expert® software (11 version) and the F-value,

Table 1
Coded independent variables values and Response Surface Methodology symbols for the optimization of the production process of maize snacks based on the CIELAB space color parameters (L^*, a^* and b^*) values, water contents and HMF formation through a Box-Behnken design*.-

Run	Production process parameters			Response variables				
	Code and decoded variables							
	X_1 Water addition (g)	X_2 Toasting time (min)	X_3 Toasting temperature (°C)	Y_1 L[a]	Y_2 a[a]	Y_3 b[a]	Y_4 Water content (%, d.b.)	Y_5 HMF (ppm)
1	(0) 9	(-1) 7	(-1) 200	72.3 ± 0.2	19.4 ± 0.2	70.57 ± 0.04	9 ± 1	3 ± 1
2	(1) 12	(0) 9.5	(1) 270	60.9 ± 0.4	23.8 ± 0.2	60.5 ± 0.7	4 ± 1	64 ± 3
3	(-1) 6	(1) 12	(0) 235	24.86 ± 0.04	15.3 ± 0.2	15.2 ± 0.3	0.7 ± 0.1	162 ± 5
4	(-1) 6	(0) 9.5	(-1) 200	68.1 ± 0.2	24.91 ± 0.05	70.5 ± 0.3	6.1 ± 0.5	10.3 ± 0.6
5	(1) 12	(-1) 7	(0) 235	71.2 ± 0.2	23.9 ± 0.2	72.8 ± 0.3	3 ± 1	8.6 ± 0.7
6	(1) 12	(1) 12	(0) 235	54.0 ± 1.8	27.8 ± 0.5	55.9 ± 0.8	0.8 ± 0.2	57 ± 5
7	(-1) 6	(-1) 7	(0) 235	69.1 ± 0.2	26.41 ± 0.01	72.11 ± 0.08	2.0 ± 0.3	21 ± 3
8	(0) 9	(0) 9.5	(0) 235	68.9 ± 1.5	31.3 ± 0.9	62.8 ± 0.5	2.1 ± 0.4	28 ± 4
9	(0) 9	(0) 9.5	(0) 235	69 ± 1	32.1 ± 0.1	62.6 ± 0.7	1.9 ± 0.1	27.8 ± 0.6
10	(0) 9	(1) 12	(-1) 200	71.6 ± 0.5	25.63 ± 0.02	67.0 ± 0.3	4.8 ± 0.6	10.14 ± 0.01
11	(1) 12	(0) 9.5	(-1) 200	77.9 ± 0.2	18.6 ± 0.1	56.9 ± 0.2	4.4 ± 0.2	3.9 ± 0.7
12	(0) 9	(-1) 7	(1) 270	70.2 ± 1.2	23.5 ± 0.5	69.0 ± 0.8	1.9 ± 0.1	32 ± 3
13	(0) 9	(0) 9.5	(0) 235	67.6 ± 0.9	31.4 ± 0.1	63.7 ± 0.9	2.3 ± 0.5	28 ± 4
14	(0) 9	(1) 12	(1) 270	19 ± 1	9.4 ± 0.7	6.0 ± 0.2	1.8 ± 0.3	212 ± 3
15	(-1) 6	(0) 9.5	(1) 270	30.4 ± 0.4	6.76 ± 0.03	7.6 ± 0.2	0.44 ± 0.02	178 ± 2

[a] All results are expressed as mean values ± standard deviation ($n = 3$).

respectively.

2.4. Color evaluation

Maize snacks color evaluation was performed by image analysis following the method reported by Agudelo-Laverde, Schebor, and Buera (2013) and Cueto, Farroni, et al. (2017) through a computer vision system (CVS). The acquired color images were obtained in Lab values through Adobe Photoshop CS6 software (Adobe Systems Inc., Berkeley, CA). Lab values were converted to the standard CIELAB space color parameters (L^*, a^* and b^*) by equations described by Yam and Papadakis (2004), as follows:

$$L^* = \frac{L}{255}\, x\, 100 \quad (2)$$

$$a^* = \frac{240a}{255} - 120 \quad (3)$$

$$b^* = \frac{240b}{255} - 120 \quad (4)$$

L^* indicates lightness and varies from 0 (black) to 100 (white) while a^* and b^* are chromatic components with values from −120 to +120 and stand for greenness (−)/redness (+) and blueness (−)/yellowness (+), respectively.

The color difference in the CIELAB space ($\Delta E_{ab}{}^*$) was calculated as:

$$\Delta E_{ab}{}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (5)$$

Where ΔL^*, Δa^* and Δb^* are the difference between the measured L^*, a^* and b^* values for each sample and the corresponding values for the raw grits ($L_g{}^* = 64$, $a_g{}^* = 19$, and $b_g{}^* = 65$), taken as a reference.

2.5. Final water content determination

Maize snacks were grinded using a Butt mill (Section 2.2) and 1 g of sample was heated in an oven at 105 °C during 24 h until constant weight. Water content (%, d.b.) was determined by weight difference.

2.6. Quantification of 5-hydroxymethyl-2-furfural (HMF)

Maize snacks were treated following the method proposed by Ameur, Trystram, and Birlouez-Aragon (2006). Briefly, 1 g of the grinded sample was suspended in 10 mL of milli-Q water and added with 2.5 mL of 40% (w/v) TCA solution. After stirring for 5 min, the mixture was adjusted to 25 mL final volume with milli-Q water and centrifuged at 3,220 g for 5 min at 25 °C. An aliquot of 200 μL was taken and filtered through a 0.45 μm nylon filter (Waters Corporation, Milford, MA). Finally, 10 μL were injected in the HPLC system for HMF determination.

An Alliance HPLC system equipped with a diode array detector (DAD) Waters 2995 (Waters Corporation, Milford, MA) was used for HMF quantification. A 2.1 mm × 100 mm Waters X-Bridge C_{18} column (Waters Corporation, Milford, MA) of 3.5 μm particle diameter operating at 25 °C was used for compounds separation. Mobile phase consisted in a 5:95 (v/v) acetonitrile-water solution over a linear gradient of 20 min with a flow rate of 0.1 mL min^{-1} (Favre et al., 2020). Calibration curve was obtained from HMF solutions in the range 0.02–23 ppm ($R^2 = 0.9999$). The absorbance was monitored at 284 nm and under these conditions HMF presented a retention time of 7.4 min (Cueto, Pérez Burillo, et al., 2017).

2.7. Optimization and verification of the model

The desirability function Derringer and Suich (1980) was used to optimize multiple responses for obtaining the combination of the independent variables that led to the commitment levels of the evaluated responses:

$$D = (d_1(Y_1)\cdot d_2(Y_2)\ldots d_i(Y_i))^{1/i} \quad (6)$$

Where $d_i(Y_i)$ are the normalized values (from 0 to 1) of each studied response. The applied criteria for optimization were minimizing HMF formation to reduce thermal damage, achieving low final water contents to assure storage stability (3–8%, d.b.) but maintaining adequate color characteristics: L^* values between 45 and 55, a^* values between 10 and 30 and b^* values between 35 and 50. These values are in line with those reported for other maize-based snacks, which were also related with their sensory acceptance ((Cueto, Farroni, et al., 2017; Cueto, Pérez Burillo, et al., 2017); Farroni & Buera, 2012; González, Loubes, & Tolaba, 2018; Sumithra & Bhattacharya, 2008). The numerical optimization resource of Design-Expert® software (11 version) provided a combination point where D is maximized. To verify the adequacy of the model for predicting the values of the responses in the combination point provided for the maximum D, maize snacks were prepared following the given conditions by the model. The responses were measured and then compared with the predicted values. The adequacy of the model was evaluated through the coefficient of variation (CV), as follows:

$$CV = \frac{\Delta X}{\overline{X}} \times 100 \tag{7}$$

Where ΔX indicates the difference between the observed and predicted values and $\overline{X}$ is the mean value of the experimental determination.

2.8. Statistical analysis

All samples were analyzed in triplicates and mean ± standard deviation results are shown for each determination. An analysis of variance (ANOVA) was performed for establishing statistical differences among samples (p-value < 0.05). Similarly, Pearson correlation coefficients and p-values were determined for evaluating correlations and their respective significance. All graphs were made using Design-Expert® software (11 version).

3. Results and discussion

3.1. Mathematical models for CIELAB color parameters

Table 1 shows the measured values of the response variables at every combination of the independent variables. Equations (8)–(10), in coded level, were obtained to describe the effects of the independent variables on L^*, a^* and b^* of maize snacks, respectively:

$$L^* = 68.47 + 8.94X_1 - 14.19X_2 - 13.71X_3 + 6.78X_1X_2 + 5.18X_1X_3 - 12.67X_2X_3 - 6.30X_1^2 - 7.38X_2^2 - 2.86X_3^2 \tag{8}$$

$$a^* = 31.60 + 2.58X_1 - 1.90X_2 - 3.14X_3 + 3.76X_1X_2 + 5.85X_1X_3 - 5.08X_2X_3 - 4.62X_1^2 - 3.65X_2^2 - 8.46X_3^2 \tag{9}$$

$$b^* = 63.04 + 10.08X_1 - 17.56X_2 - 15.22X_3 + 10.01X_1X_2 + 16.61X_1X_3 - 14.85X_2X_3 - 6.67X_1^2 - 2.40X_2^2 - 7.50X_3^2 \tag{10}$$

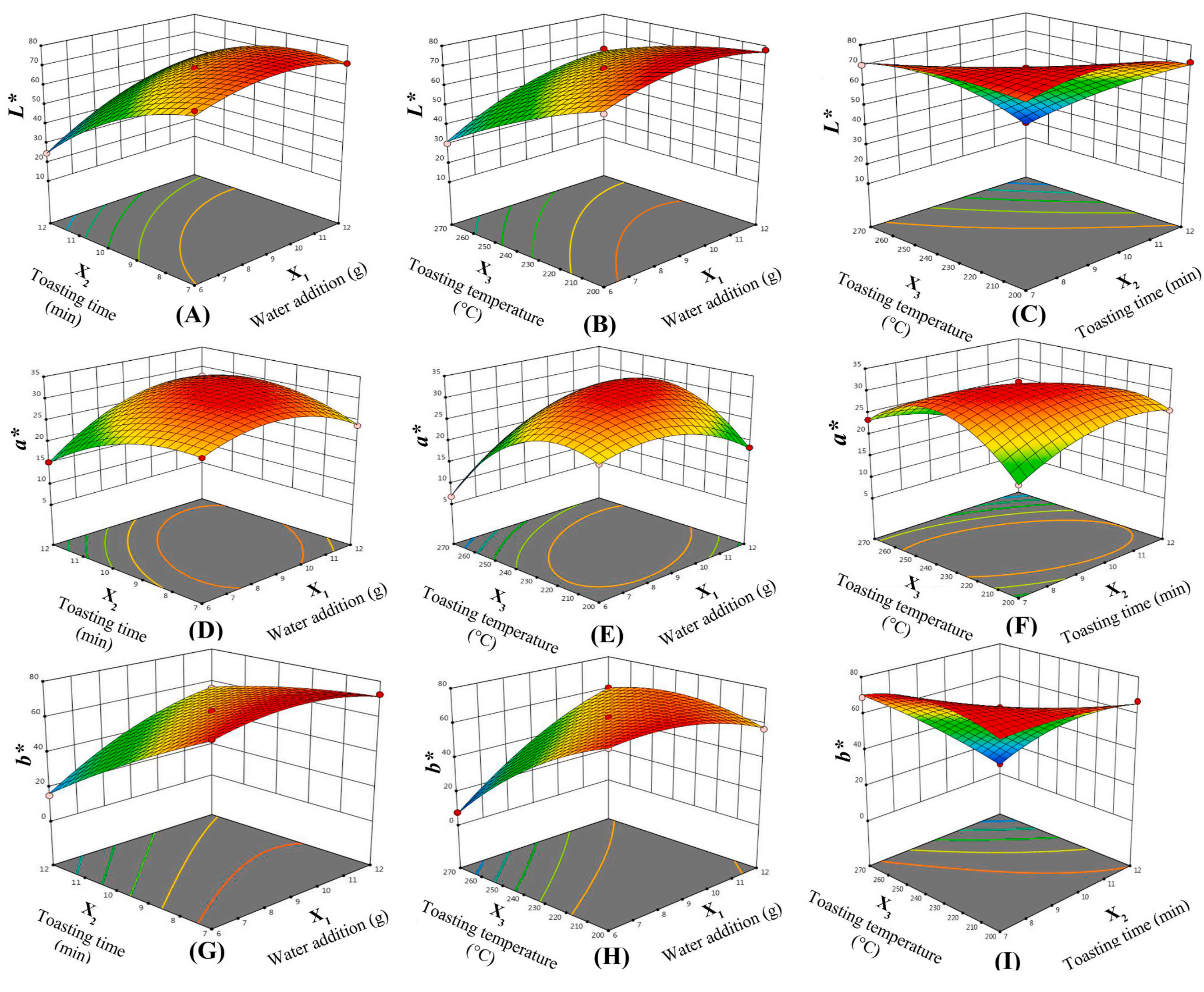

Fig. 1. Response surface plots of CIELAB space color parameters values (L^* **(A–C)**; a^* **(D–F)** and b^* **(G–I)**) of maize snacks as a function of the combination of the independent variables. **(A)**, **(D)** and **(G)** combine water addition (g) and toasting time (min) with 235 °C as toasting temperature; **(B)**, **(E)** and **(H)** combine water addition (g) and toasting temperature (°C) with 9.5 min as toasting time; **(C)**, **(F)** and **(I)** combine toasting time (min) and toasting temperature (°C) with 9 g of water addition. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Where X_1 is the water addition (g/15 g maize flour), X_2 is the toasting time (min) and X_3 is the toasting temperature (°C) (Table 1). The regression coefficients (R^2) were 0.9956, 0.9993 and 0.9988 for L^*, a^* and b^*, respectively (Supplementary File S.1), indicating a good fit to experimental values (Gümüşay et al., 2019). All terms in Equations (8)–(10) were significant for modeling the color parameters.

At higher levels of water (X_1), maize snacks remained with a lighter, yellowish color, indicating lower development of non-enzymatic browning reactions, while larger toasting times (X_2) or higher toasting temperatures (X_3) favored samples darkening and browning. The modifications of the chromatic parameters could be directly linked to the development of the Maillard reaction (Cueto, Farroni, et al., 2017; Cueto, Pérez Burillo, et al., 2017; Mesías et al., 2019; Nguyen et al., 2016). Moreover, non-enzymatic browning is favored by starch dextrinization that is known to take place above 200 °C in cereal-based systems (Singh, Okadome, Toyoshima, Isobe, & Ohtsubo, 2000). These reactions are promoted by the combination of long toasting time and high temperature (X_2X_3) and the consequent browning was reflected in the decrease of the reflectance values (Cueto, Pérez Burillo, et al., 2017; Farroni & Buera, 2012; Sumithra & Bhattacharya, 2008).

The effects of the combined processing conditions on the chromatic parameters could be better analyzed from the plots presented in Fig. 1. In these 3D plots a response is predicted using two independent variables while the third is set to the center value of its range. Lightness (L^*) considerably diminished at increasing toasting time (X_2), particularly at low amounts of added water (X_1), from which L^* values of about 70 for the raw samples (which means a lighter color) dropped to values in the range of 25–30 (Fig. 1A). On the contrary, L^* remained high (60 and above), at short or medium toasting times (7–9 min), especially as higher was the initial added water. From the observation of the slope of this response surface, water addition had a predominant effect on L^* values over toasting time in the studied ranges, in agreement with Equation (8): higher L^*values were obtained at higher water addition levels. Also, samples became darker with increasing toasting temperature, especially at low levels of initial water (Fig. 1B). The combined effects toasting temperature (X_3) and time (X_2) negatively influenced lightness (Fig. 1C). Carefully observing the behavior of chromatic values along the X_1 axis it can be noticed that it shows a maximum, especially at low toasting time or temperature, which is more evident in the variable b^* (Fig. 1D–F). At very low water levels, at which molecular movement is restricted, the non-enzymatic browning reactions development is limited. From this point, by increasing water content, browning reactions rate increases because of the favored reactants mobilization (Acevedo, Schebor, & Buera, 2008). On the other hand, water, as a product of the reaction, delays its progress (Agudelo-Laverde et al., 2013) and thus, further increase in water content produces a reduction of non-enzymatic browning.

It is to be noted that while L^* decreased continuously as temperature or time increased, the chromatic variables a^* (representing reddish coloration) and b^* (representing yellowish coloration) showed maximum values in the intermediate studied ranges of temperature and water content (Fig. 1 D-F and 1 G-I, respectively). At the studied conditions there were optimum values of water content and temperature for browning development. It is known that, depending on its content, water may favor or inhibit the development of non-enzymatic browning reactions (Farroni & Buera, 2012; Farroni et al., 2008; Gómez-Narváez et al., 2019; Van Der Fels-Klerx et al., 2014). This double effect of initial water level was evident on the chromatic components a^* and b^* (Fig. 1 D-E and 1 G-H, respectively) rather than on L^* values, because a continuous lightness decrease occurs during the reaction, while the chromatic components achieved maximum values. While L^* values decreased with increasing temperature (Fig. 1B and C) the variables a^* and b^* showed maximum values at intermediate temperature values (Fig. 1 E-F and H–I, respectively), which is related to the complex interaction of the variables water content and temperature, as will be discussed later.

3.2. Mathematical model for final water content

Equation (11), including only the significant terms in coded level, was used to analyze the effects of the independent variables on the final water content (WC, %, d.b.) of maize snacks:

$$WC\ (\%,\ d.b.) = 1.80 + 0.2862X_1 - 0.9663X_2 - 2.08X_3 + 1.19X_1X_3 - 1.04X_2X_3 + 2.19X_3^2 \quad (11)$$

The regression coefficient (R^2) of the model was 0.9531 (Supplementary File S.1) and the terms X_1X_2, X_1^2 and X_2^2 were not significant for predicting the WC of maize snacks.

The modifications of final WC due to the combined processing conditions are shown in Fig. 2. Final WC was lower as lower was the added water and as higher was the toasting temperature. Increasing toasting temperature increased the driving force for water evaporation, which was evidenced in the rapid slope reduction along the X_3 axis. This negative slope was higher than the slope in the time axis indicating that temperature effects prevailed over time in reducing water content (Fig. 2A). As temperature reached 270 °C water content was becoming less dependent on the toasting time, indicating that all water that could evaporate was lost in less than 7 min (Nguyen et al., 2017; Van Der Fels-Klerx et al., 2014). As the samples continued to be exposed to high temperatures during several minutes, browning was favored and L^*, a^* and b^* values further decreased, as discussed in the previous section.

On the other hand, final WC was higher as higher was the level of added water, even at the highest toasting temperature tested (Fig. 2B). That is, it took more time to evaporate the initial water, as it was higher, even though the rise in temperature accelerated the process. This effect was reflected in the positive term X_1X_3 on Equation (11).

3.3. Mathematical model for HMF formation

Equation (12), in coded level, described the effects of the independent variables on HMF (ppm) formation:

$$HMF\ (ppm) = 27.27 - 29.81X_1 + 47.01X_2 + 57.29X_3 - 23.17X_1X_2 - 27.01X_1X_3 + 43.19X_2X_3 + 17.27X_1^2 + 17.73X_2^2 + 19.40X_3^2 \quad (12)$$

The obtained regression coefficient (R^2) was 0.9999 (Supplementary File S.1) and all terms were significant. X_1 and the interactions X_1X_2 and X_1X_3 had negative effects, while X_2, X_3, the interactions X_2X_3 and the quadratic terms X_1^2, X_2^2 and X_3^2 promoted the formation of HMF in the snacks.

The effects of the combined processing conditions on HMF development could be observed in Fig. 3. Increasing either toasting temperature or time increases HMF content. This increment was slowed down as initial water content increases (Fig. 3A and B). It is to be noted that the formation of HMF occurs through dehydration reactions, thus, water, as a product of the reaction, delays its progress (Agudelo-Laverde et al., 2013). The combination of higher toasting time and temperature along with the lowest initial water content produced the highest HMF

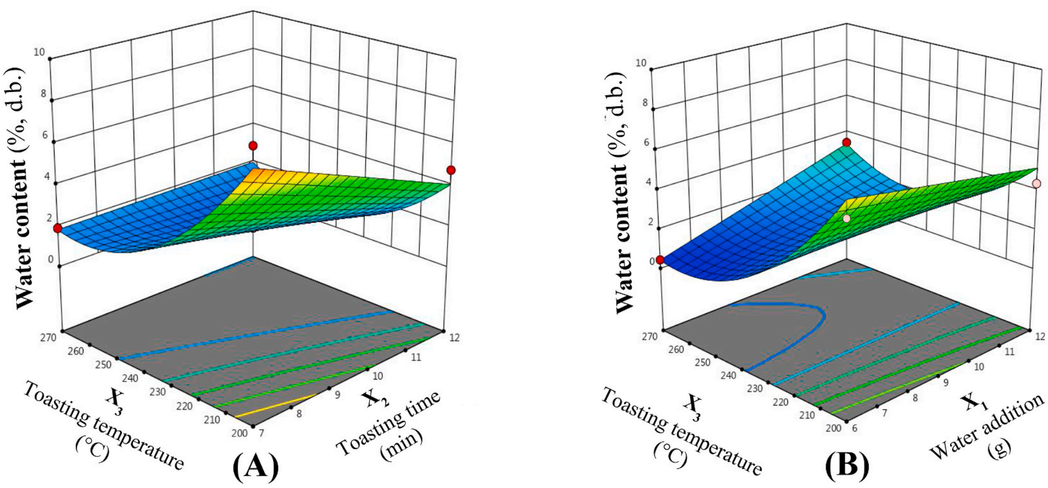

Fig. 2. Response surface plots of water contents (%, d.b.) of maize snacks as a function of the combination of the independent variables: **(A)** toasting time (min) and toasting temperature (°C) with 9 g of water addition and **(B)** toasting temperature (°C) and water addition (g) with 9.5 min of toasting time.

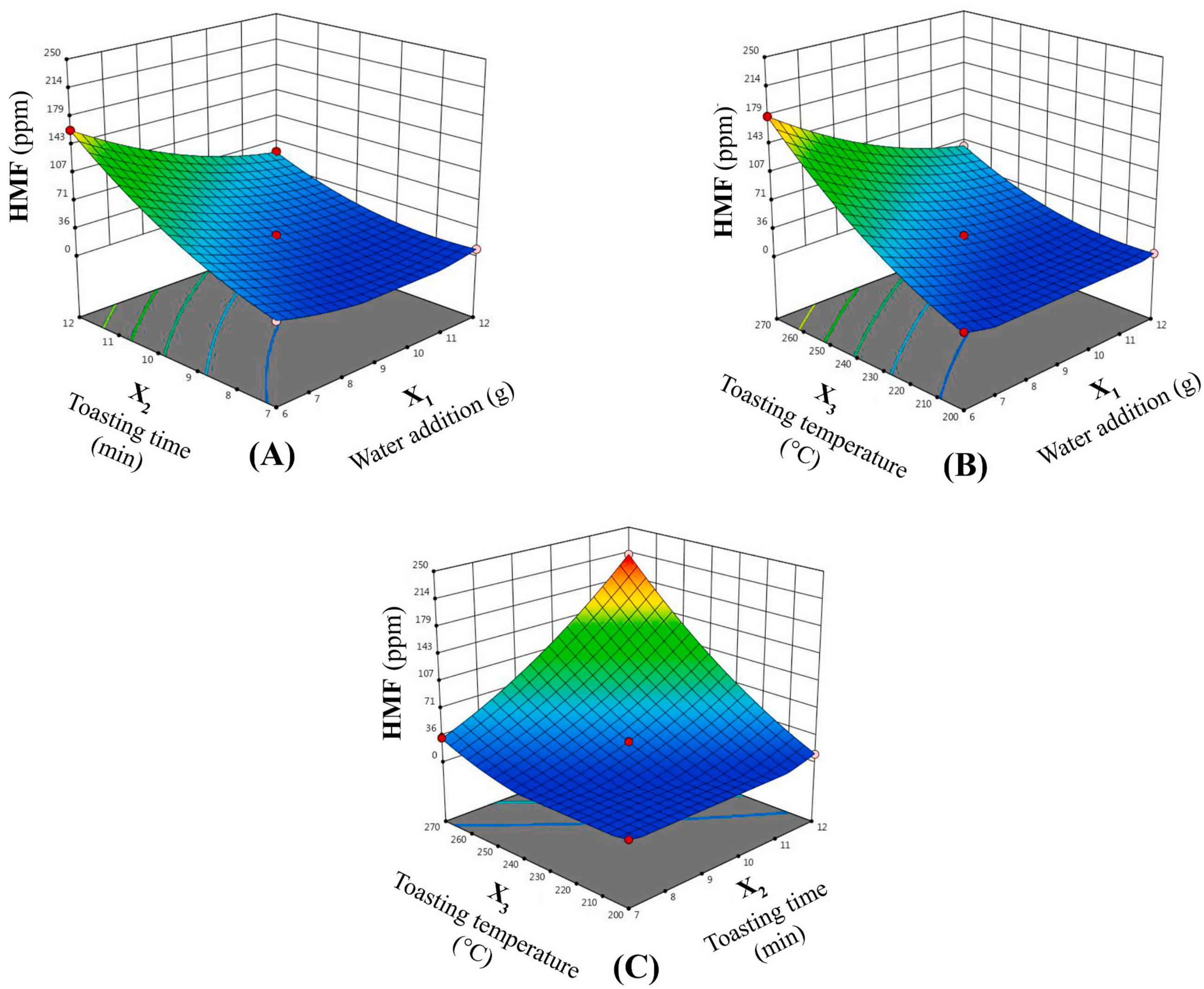

Fig. 3. Response surface plots of HMF contents (ppm) of maize snacks as a function of the combination of the independent variables: **(A)** water addition (g) and toasting time (min) with 235 °C as toasting temperature; **(B)** water addition (g) and toasting temperature (°C) with 9.5 min as toasting time and **(C)** toasting time (min) and toasting temperature (°C) with 9 g of water addition.

content, and thus the highest thermal damage on the product. The effects of toasting time and temperature prevailed over the influence of water content, which is particularly noticeable in Fig. 3C. In this graph, the lag phase in HMF formation described by Nguyen et al. (2017, 2016) and Van Der Fels-Klerx et al. (2014) could also be observed. Considering that HMF formation occurs through dehydration steps, this lag phase may be explained by the necessity of eliminating certain amounts of water prior to the formation of HMF. Moreover, water elimination and samples exposition to high temperature during several minutes favors starch dextrinization. As a result, HMF precursors such as dextrins and sugars are formed, which explains the exponential accumulation of HMF (Giovanelli & Cappa, 2021; Gökmen et al., 2007; Van Der Fels-Klerx et al., 2014). The point of maximum HMF concentration (212 ppm) is coincident with the lowest chromatic values ($L^* = 19$; $a^* = 9.4$; $b^* = 6.0$, Table 1) and hence the darkest sample. These results confirm the relationship between non-enzymatic browning reactions and samples chromatic attributes in these systems (Gómez-Narváez et al., 2019).

3.4. Optimum conditions, D function and model validation

D function was used to determine the optimum variables combination that led to maize snacks with minimum HMF formation, while maintaining adequate color characteristics and low final water contents, as mentioned in section 2.7. The combination of adding 6 g of water to 15 g of maize flour before cooking and toasting at 217 °C during 11 min presented D = 0.705. At these conditions, the resulting snacks may present 3% of final water content (d.b.), with CIELAB color parameters values of $L^* = 53$, $a^* = 24$ and $b^* = 50$, and 65 ppm of HMF as predicted responses. These parameters are in the same range of other sensory accepted cereal-based products (Cueto, Pérez Burillo, et al., 2017; Ghazouani et al., 2021; González et al., 2018; Mesías et al., 2019; Morales et al., 2020; Van Der Fels-Klerx et al., 2014).

For verifying the model's utility, CV between the predicted and experimental values were calculated and results were: 6.06%, 2.68%, 5.17%, 7.12% and 1.26% for L^*, a^*, b^*, final water content and HMF, respectively. The low CV values obtained confirmed that RSM is a suitable tool to simultaneously optimize multiple response variables in the definition of maize snacks' process parameters and production design (Favre et al., 2020; Gümüşay et al., 2019).

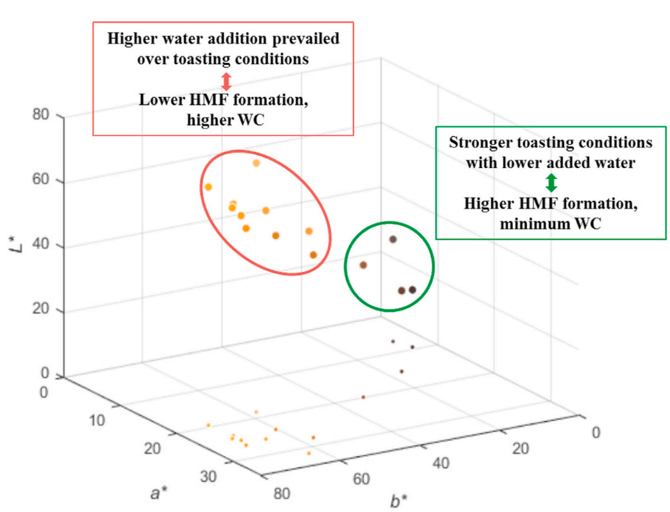

Fig. 4. Relationships between processing conditions water addition, toasting time and temperature and response variables CIELAB space color parameters, final water content and HMF formation in maize snacks. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.5. General discussion

The combination of the analyzed processing conditions led to modifications of the response variables: higher levels of water addition promoted lighter colors, manifested by the higher reflectance values of the CIELAB color parameters, higher final water contents and minimum HMF formation. On the contrary, longer toasting times and higher temperatures promoted samples darkening and higher formation of HMF, along with lower final water contents. These relationships are analyzed in Fig. 4. Conditions leading to low L^* values and changes of chromaticity (a^* and b^* values) were related to specific stages of non-enzymatic browning development. According to Pepa, Rodríguez, dos Santos Ferreira, and Buera (2020), color displacement during browning process occurred in three different stages. During the first step, samples turned slightly yellow (b^* increased). Then, samples color turned towards red (a^* increased) and finally, the chromatic parameters decreased (due to a reflectance decrease), and darkening prevailed, being the changes at this stage represented only by L^* values in the very dark samples. Fig. 4, which presents data of the combination of the three CIELAB parameters, shows that samples become darker following a spiral trajectory, with higher variation of the chromatic variables a^* and b^* at milder treatment conditions and with lower L^* values and the corresponding displacements with stronger toasting conditions (Pepa et al., 2020). As shown in Fig. 4, the way the CIELAB color parameters change with processing conditions agree with this typical chromatic behavior expected for the development of Maillard reaction (Cueto et al., 2015; Farroni & Buera, 2012; Pepa et al., 2020).

The relationship between the formation of HMF and non-enzymatic browning degree was analyzed in maize snacks through the chromatic variables. The results, including the fitting equations and parameters, are shown in Fig. 5 (A-D). Good linear negative correlations could be established between HMF concentration and L^* values and with the chromatic variable b^* (Fig. 5 A and C, respectively), with $R^2 = 0.97$ in both cases. This behavior is related to the darkening process, which promotes a constant decrease of lightness (L^*), but also of yellowness (b^*), that is related to the lightest hues. However, the behavior of the a^* variable (redness), shown in Fig. 5B, presented a bell shape which indicated that the initial redness development decreased only at high darkening degrees (due to the whole reflectance decrease). On the other hand, as shown in Fig. 5D, a poor correlation was found between ΔE_{ab}^* and HMF content. For instance, when a sample is darkening, the L^* and b^* values decrease while a compensation occurs when the a^* values increase (as shown in Fig. 5B), which is reflected in the ΔE_{ab}^* values, inducing to misinterpretations. These correlations indicate that maize snacks' darkening and yellowish colorations (L^* and b^* values) could be used as heat-induced changes or damage indicators. These results provided a deeper understanding of the non-enzymatic browning reaction rate and the associated modifications of visual aspects.

4. Conclusions

The optimization of maize snacks production process could be successfully achieved by means of RSM through the evaluation of physical and chemical properties of interest. The combination of the processing conditions directly affected the analyzed response variables: toasting low water-containing samples during large times at high temperatures generated dry maize snacks with low L^* and b^* values but with high a^* values, due to the development of non-enzymatic browning reactions, confirmed by the amount of HMF. The defined optimum conditions (6 g of water addition, 11 min of toasting time at 217 °C) led to obtaining products with minimized HMF formation (64 ppm), adequate color parameters ($L^* = 50$, $a^* = 25$, $b^* = 47$) and low water content (3.2%, d.b.) to assure storage stability. It is to be noted that the color difference in the CIELAB space, ΔE_{ab}^*, has been frequently employed as an index of color evolution in non-enzymatic browning reactions. However, ΔE_{ab}^* represents a distance in the CIELAB space and it is not informative of the

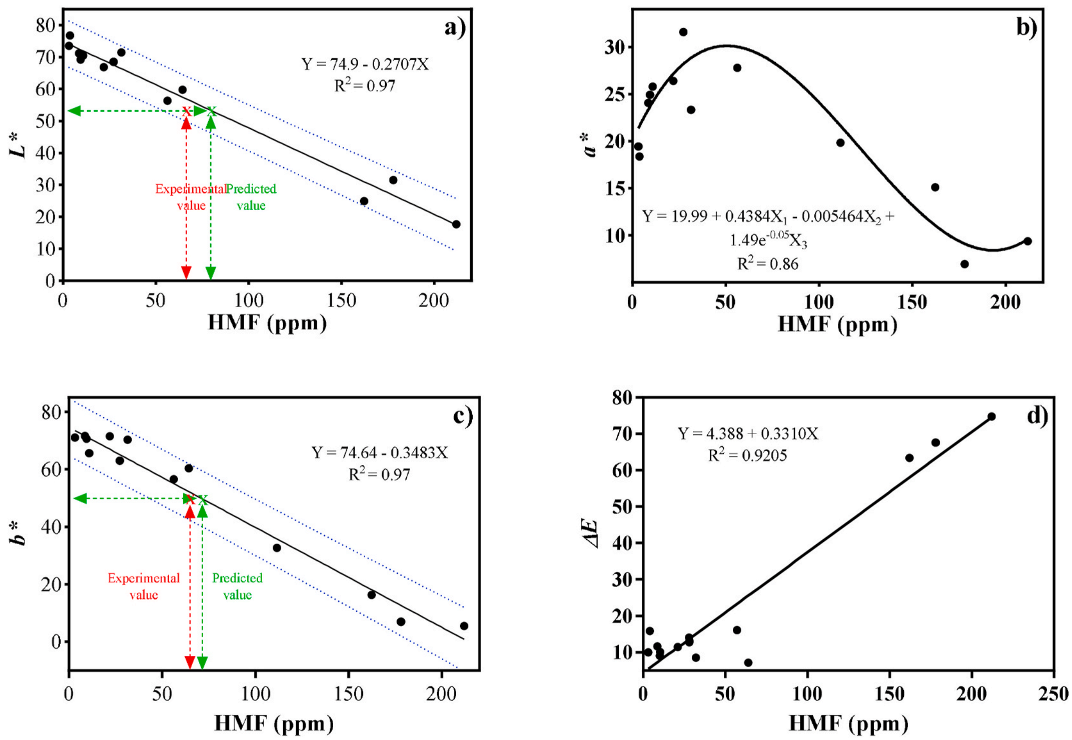

Fig. 5. Correlations between HMF formation (ppm) and L^* **(a)**, a^* **(b)**, b^* **(c)** and ΔE **(d)** values in maize snacks.

kind of color change that is occurring. On the light of the data presented, its use has to be discouraged if the direction of the color displacement is required. Moreover, the correlation between L^*, b^*, and HMF values in the obtained snacks can be used to predict heat damage through simple, practical, and non-destructive determinations.

CRediT authorship contribution statement

Guido Rolandelli: Formal analysis, Investigation, Data curation, Writing – original draft. **Leonardo Cristian Favre:** Formal analysis, Data curation, Methodology, Writing – original draft. **Ndumiso Mshicileli:** Methodology, Validation. **Lusani Norah Vhangani:** Resources, Methodology. **Abel Eduardo Farroni:** Data curation, Formal analysis, Funding acquisition, Writing – original draft. **Jessy van Wyk:** Funding acquisition, Project administration. **María del Pilar Buera:** Funding acquisition, Project administration, Resources, Visualization, Writing – original draft.

Declaration of competing interest

All authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2021.111636.

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