TITLE: Physicochemical characteristics as the markers in predicting the self-life of gluten-free cookies

AUTHORS: Mladenka Pestorić, Marijana Sakač, Lato Pezo, Dubravka Škrobot, Nataša Nedeljković, Pavle Jovanov, Olivera Šimurina, Anamarija Mandić

NOTICE: This is the author's version of a work that was accepted for publication *Journal of Cereal Science.* Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Journal of Cereal Science*, Volume 77, September 2017, Pages 172–179. DOI: 10.1016/j.jcs.2017.08.013

Physicochemical characteristics as the markers in predicting the self-life of gluten-free cookies

Mladenka Pestorić[1], Marijana Sakač[1], Lato Pezo[2*], Dubravka Škrobot[1], Nataša Nedeljković[1], Pavle Jovanov[1], Olivera Šimurina[1], Anamarija Mandić[1]

[1]University of Novi Sad, Institute of Food Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

[2]University of Belgrade, Institute of General and Physical Chemistry, Studentski trg 12/V, 11000 Beograd, Serbia

Running head: Shelf-life prediction of gluten-free cookies

Tel: +381 6380 08 753

Fax: +381 21 450 730

E-mail address: latopezo@yahoo.co.uk

Abstract

The objective of this study was to investigate the effect of different storage conditions on physicochemical stability assessment of gluten-free rice-buckwheat cookies. Second order polynomial (SOP) models were developed to explore the effects of storage time (0-6 months), at ambient (23 ± 1 °C) and elevated (40 ± 1 °C) temperature, packaging condition (packed and unpacked samples), and cookie surface position on the level of water activity (a_w), hydroxymethylfurfural content, peak force, and colour parameters (L*, a*, b*, h*, C*, ΔE*). The chemical characteristics of cookies were influenced by temperature, while the colour properties were mostly influenced by the position of the sample surface. The firmness was affected upon the synergy effect of temperature and packaging condition. The performance of the developed SOP models was to investigate the effect of storage conditions on the observed parameters, which showed a good fit to the experimental ($r^2 > 0.8$). The obtained results demonstrated that the developed empirical models gave an appropriate fit to experimental data and predicted the physicochemical properties at a satisfactory level, and that they could be successfully implemented to cookie stability assessment.

Key words: gluten-free cookies, physicochemical stability, mathematical modelling

1. Introduction

Considering cereals and health, it is important to notice that an increasing percentage of the population shows intolerance to gluten intake like celiac disease patients. The symptoms are triggered by gluten – specific proteins in wheat, spelt, barley, rye, and oat. In celiac disease, the body's immune system responds abnormally to gluten, resulting in inflammation and damage to the lining of the small intestine, and reduced absorption of iron, calcium, vitamins A, D, E, K, and folate. In this case, the beneficial treatment is a dietary therapy, avoiding the intake of gluten-containing foods (Rosell et al., 2015). Development of gluten-free baked goods remain a technological challenge, largely because of sensory changes that result from the absence of gluten (da Silva and Conti-Silva, 2016). To imitate the viscoelastic properties of gluten, a large number of flours (rice, buckwheat, corn, millet, amaranth, quinoa, and/or sorghum) (Torbica, et al., 2010; Sakač, et al., 2015) or some other ingredients (Dapčević Hadnađev, et al. 2013) have been utilized for gluten-free product development, resembling the composition, structure, mouthfeel, and acceptance of gluten-containing products. Among these products, the short dough cookie is widely consumed throughout the world and represents one of the largest food category, primarily due to its versatility, convenience, and attractive sensory attributes (Pestorić, et al., 2015), but especially because of its long shelf life. Storage stability of cookies, as for many baked products, could be defined as maintenance of sensory and physicochemical properties (appearance, freshness or moistness, colour, firmness etc.) by preventing alteration associated with staling or some other process, i.e. lipid oxidation during storage (Baixauli, et al., 2008).

Predictive shelf life modelling is still an important field of research and a significant advance of models and unique software may be expected in the near future. The term 'predictive stability' is maybe relatively new to the scientists, but the concept of mathematical modelling of chemical responses to environmental conditions is surely not. In recent years, predictive stability has become a plentiful area for research and software application. Multifunctional models can be easily used by food scientists (Turan, et al., 2015), because they are able to quantify the interactions between two or more factors and allow the interpolation of factor combinations. Their utilization can also help to reduce the needs for storage trials, challenge tests, and process modifications, which are time-consuming and expensive (Blackburn, 2000).

It is already known that physical changes, sometimes coupled with subsequent chemical reactions, limit product shelf life (Yang, et al., 2013). Therewithal, it was found that most of the biochemical and microbiological reactions are controlled by water activity, which can be used as a useful indicator to predict product stability. Moreover, colour can be used as an indicator for arranging different biochemical reactions and changes over the sustainability of the product (Wibowo, et al., 2015). Most published work dealing with cookie texture described the variation in cookie break strength under different conditions(Jacob and Leelavathi, 2007). In addition, compounds like 5-hydroxymethyl-2-furfural can be useful in monitoring changes during cookie storage (- , et al., 2010). However, HMF is considered as an undesirable compound and to be a good indicator of quality deterioration due to excessive heating or storage for a wide range of carbohydrate-containing foods such as cookies(van Der Fels-Klerx, et al., 2014).

Our previous study (Sakač, et al., 2016) showed the possibility to predict the shelf life of the unpacked and packed gluten-free rice-buckwheat cookies kept at ambient (23 ± 1 °C) and elevated (40 ± °C) temperature during storage, by measuring off-flavour volatile compounds (aldehydes), antioxidant capacity, total phenolic, rutin content, and evaluating sensory properties. Based on the obtained results, the evaluated sensory attributes were suggested to be relevant parameters for predicting the endpoint of the cookie shelf life. Despite the fact that sensory evaluation of changes occurring during cookie storage was the essential measure of perceived quality, it is still an expensive and time-consuming tool to perform. Therefore, physicochemical parameters may play a crucial role in stability testing as they can be used either to predict the endpoint of cookie shelf life, or to confirm the results obtained by the sensory panel.

Because of the above mentioned facts, the focus of this study was to investigate the physicochemical stability of the gluten-free rice-buckwheat cookies during storage. Moreover, the main goal was to investigate the influence of temperature, storage time and packaging on water activity, hydroxymethyl furfural, firmness, and colour parameters, by using the SOP models as an effective tool for optimizing a variety of storage processes.

2. Materials and Methods

Cookies were prepared as shown in Fig.1. The base recipe was formulated with rice flour, light buckwheat flour, diacetyl tartaric acid esters of monoglycerides (DATEM) from InCoPa GmbH, Munich, Germany, carboxymethyl cellulose sodium salt (CMC) from Alfa Aesar GmbH, Karlsruhe, Germany, vegetable fat originating from refined palm and sunflower oil (Puratos NV, Groot-Bijgaarden, Belgium), granulated sugar, granulated salt, honey, and deionized water. Flour, salt, sugar, DATEM and CMC were sifted together and mixed for 2 min. Subsequently, honey, vegetable fat, and water were added and mixed for additional 25 min. The dough was prepared by mixing the ingredients in a farinograph mixing bowl (Brabender, Duisburg, Germany), at 30 °C. The prepared cookie dough was rested for 24 h at 8 °C in a refrigerator to make hydration of the added CMC. Afterward, the dough was tempered to room temperature and laminated to a thickness of 4 mm with pilot scale laminator dough (Mignon, Italy). Cookies were shaped using a stainless cutter mould (60×55 mm) and baked at 170 °C for

12 min in a laboratory oven (MIWE gusto® CS, Germany). The baked cookie samples were cooled for 2 h at room temperature. Under atmospheric conditions and using a laboratory vacuum sealer, one batch of the baked cookies was packed into 40 mm polypropylene (OPP/OPP) bags, which gas permeability was 3858.9 mL/m^2 24 h, 1 bar for CO_2, 1236.3 mL/m^2 24 h, 1 bar for N_2, and 418.9 mL/m^2 24 h, 1 bar for air (Sakač, et al., 2015; Sakač, et al., 2016). Another batch of cookies was not packed. Both batches of cookies, packed and unpacked, were stored in parallel at two temperatures, at room temperature (23 ± 1 °C) and at 40 ± 1 °C in the climate chamber (Blinder, Tulttingem, Germany). The storage time was 6 months.

Figure 1. Cookie manufacturing and storage

2. 1. Water activity (a_w)

Water activity (a_w) was determined by an aw-meter (TESTO 650, Testo AG, Lenzkirch, Germany). About 2.5 g of a ground cookie sample was placed into the sample holder at 25 °C, and the measured a_w values of three replicates were recorded after equilibration.

2. 2. Hydroxymethylfurfural analysis (HMF)

2. 2. 1. Sample preparation

The extraction procedure was performed according to Rufián-Henares, et al. (2006), with the modifications which were done by Petisca et al. (2014). Ten grams of sample were suspended in 5 mL water:methanol (70:30). The mixture was thoroughly stirred during 1 min and then 2.0 mL of Carrez I and Carrez II solutions were added and centrifuged at 5000 rpm (4 °C) during 15 min, recovering the supernatant to a 15 mL flask. Two more consecutive extractions were made with 2 mL of water:methanol (70:30) until collecting 10 mL of supernatant. Two millilitres of this solution was centrifuged at 8000 rpm for 15 min before being analysed.

2. 2. 2. HPLC-DAD analysis

The chromatographic separation and quantification of HMF was performed using the HPLC method described by Ariffin, et al. (2014), with some modifications. The extracts were filtered through 0.45 μm pore size nylon filter (Agilent Technologies, Santa Clara, CA, USA) before injection into the HPLC system. Liquid chromatograph (Agilent 1200 series), equipped with a DAD detector and an Eclipse XDB-C18, 1.8 μm, 4.6 × 50 mm column (Agilent) was used for quantification of HMF in the obtained extracts. Separation of the analyte was achieved with a column temperature of 30 °C and sample injection volume of 2 μL. The mobile phase consisted of two eluents, H_2O (0.1% HCOOH) (A) and methanol (B), delivered at a flow rate of 0.75 mL/min. The isocratic elution was employed with the ratio A:B (90:10, v/v). The DAD wavelength was set at 284 nm. The total run time of the analysis was 5 min.

2. 3. Colour determination

Colour was determined by a chromameter (Minolta Co., Type CR 400, Osaka, Japan) on both surfaces (top and bottom) of the cookie samples. Because of the particle dispersion, colour quantifications were measured at five sections of the cookie (at the centre and four corners) with a minimum of ten readings per sample, and the results were averaged. Colour characteristics were presented in the CIE L*a*b* system in which L* represents lightness (L*=0 (black) and L*=100 (white)), a* represents red and green colour coordinates (-a*=greenness and +a*=redness)), while b* represents yellow and blue colour coordinates (-b*=blueness and

+b*=yellowness)). The h* (h*=arctan b*/a*), and C* ($C^* = ((a^*)2 + (b^*)2)^{0.5}$) characteristics were obtained by computation. Additionally, total colour difference, ΔE*, ($\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{0.5}$, between the starting cookie sample and the gluten-free rice-buckwheat cookies was computed ($\Delta L^* = L^* - L^*_0$, $\Delta a^* = a^* - a^*_0$, and $\Delta b^* = b^* - b^*_0$). If the total colour difference was visually obvious, the values used to determine, were the following: $\Delta E^* < 0.2$ − colour differences are not obvious to human eyes, ΔE* = (0.2 – 1) − colour difference is noticeable by the human eye, ΔE = (1 – 3) − colour difference is not appreciated by the human eye, ΔE* = (3 – 6) colour difference is well perceived by the human eye, and $\Delta E^* > 6$ – obvious variations of colour, Schläpfer, 2002.

2. 4. Textural measurement

The textural parameter of firmness was determined using a TA.XT Plus Texture Analyzer (Stable Micro Systems Ltd., Surrey, England, UK), equipped with a 3-point bending rig (HDP/3PB), and with a 5 kg load cell. Setting procedure on texture analyzer was as follows: mode-measure force in compression; pre-test speed: 1.0 mm/s; test speed: 3.0 mm/s; post-test speed: 10.0 mm/s; distance: 5.0 mm; trigger force: 50 g. Firmness, which is expressed as the peak force (F) at the time of interruption (the point of break), was determined. Ten measurements per each sample were conducted, and the results were averaged.

2. 5. Mathematical modelling and statistical analysis

The collected data were subjected to analysis of variance (ANOVA), for the comparison of means and treatment means they were separated using post-hoc Tukey's HSD test to consider significantly different means at $p<0.05$ significance level. The SOP model was fitted to the experimental data. Nine mathematical models of the following form were developed to relate nine responses (Y) and four process variables (X):

$$Y_k = \beta_{k0} + \sum_{i=1}^{4} \beta_{ki} \cdot X_i + \sum_{i=1}^{4} \beta_{kii} \cdot X_i^2 + \sum_{i=1,\, j=i+1}^{4} \beta_{kij} \cdot X_i \cdot X_j, \text{ k=1-9,} \qquad (1)$$

where: β_{k0} - the constant (intercept) coefficients, β_{ki} - the linear coefficients, β_{kii} - the quadratic coefficients, β_{kij} - the cross storage condition (interchange) coefficients are constant regression coefficients; represents the predicted response variables, either a_w, HMF, L*, a*,b*,C*, h*, ΔE* or F; Xi and Xj are the independent variables affecting the responses (X_1–storage time; X_2–temperature; X_3–packaging condition; X_4–position of cookie sample (bottom or top surface)). The adequacy of the developed models was tested using coefficient of determination (r^2), reduced chi-square (χ^2), mean bias error (MBE), root mean square error (RMSE), and mean percentage error (MPE). These commonly used parameters can be calculated as follows:

$$\chi^2 = \frac{\sum_{i=1}^{N} (x_{\exp,i} - x_{pre,i})^2}{N-n}, \quad RMSE = \left[\frac{1}{N} \cdot \sum_{i=1}^{N} (x_{pre,i} - x_{\exp,i})^2 \right]^{1/2},$$

$$MBE = \frac{1}{N} \cdot \sum_{i=1}^{N} (x_{pre,i} - x_{\exp,i}), \quad MPE = \frac{100}{N} \cdot \sum_{i=1}^{N} \left(\frac{\left| x_{pre,i} - x_{\exp,i} \right|}{x_{\exp,i}} \right) \qquad (2)$$

where $x_{exp,i}$ stands for the experimental values and $x_{pre,i}$ are the predicted values obtained by calculating from the model for these measurements. N and n are the numbers of observations and constants, respectively.

3. Results and Discussion

According to Pérez et al.(2013), influential factors can significantly affect the reactions and need to be defined during mathematical modelling. As previously posted by Schläpfer, et al. (2002), it would be desirable to generalize the models so that they include, as parameters, the factors which more strongly affect the quality loss rates and are susceptible to variation during the storage time. Assessing the reliability of the generated predictive mathematical models can be achieved by model fitting which was done and presented in the next subsections.

3. 1. Model fitting

ANOVA was conducted by StatSoft Statistica, v. 10 to show the significant effect of the independent variables to the responses, and to recognize which of the responses were significantly affected by the varying treatments and their combinations. The effects of ambient (23 ± 1 °C) and elevated (40 ± °C)) temperature (T), storage time (t) (0–6 months), and packaging (P) (separately packed and unpacked in a bulk form) on water activity (a_w), hydroxymethylfurfural (HMF) content, peak force (F), and colour parameters, were fitted to the SOP models.

As can be seen from the data in Table 1, the linear term of T was the most influential in the SOP model for a_w evaluation ($p<0.01$). It is apparent from this table that both linear terms of t and T significantly contributed ($p<0.01$) to the prediction of HMF. Further analysis showed that the nonlinear interaction of t × T also affected the a_w and HMF calculation ($p<0.01$). ANOVA also revealed that the nonlinear synergy effect of T × P was the most influential in the SOP model for force (F) assessment ($p<0.01$).

Furthermore, the effects of the storage conditions on the colour characteristics were also fitted to the SOP models. As presented in Table 2, the linear term of cookie position – at the bottom surface (P0) was the most influential in the SOP model for the assessment of all colour parameters, statistically significant at $p<0.01$ level. Moreover, the linear term of P contributed substantially to the prediction of b*, C*, and h* colour parameters ($p<0.01$), while the influence of P on the assessment of L* was statistically significant at $p<0.05$ level. The linear term of t was also influential for the a* and h* prediction ($p<0.01$), and for L* ($p<0.05$). At the same time, the linear term of T was significant for assessing the a* and h* colour parameters ($p<0.05$ level). In addition, all nonlinear interacts, such as t × T, t × P, and T × P were influential ($p<0.05$) for h* assessment, while the term T × P was important for the calculation of the L*, b*, and C* value ($p<0.01$), as well as for the assessment of the a* and h* colour parameters.

3. 2. Influence of storage conditions on the observed responses

3. 2. 1. Effects of storage condition on water activity (a_w)

The amount of aw under different storage conditions is presented in Table S1 in Supplementary material. There was a slight increase in the a_w values in both batches kept at ambient (23 ± 1 °C) temperature (Table S1). Closer inspection of the table shows that there were noticeable variations in the a_w values during storage in the packed cookie samples, and very noticeable variation in the unpacked samples, both kept at an elevated temperature (40 ± 1 °C) (Table S1). It is also apparent from this table that the a_w values were less than 0.5, indicated that could not get to microbial growth, at the same time suggesting the potential safety of the cookies during storage time, Cauvain and Young, 2008.

The influence of different storage conditions on the observed responses was additionally explained through the regression coefficients (RCs). The p-value for each term in a regression model tests the null hypothesis that the coefficient is equal to zero (i.e. it produces no effect to the response variable). If a low p-value is obtained ($p < 0.05$), it indicates that the null hypothesis should be rejected, Moore and McCabe, 2003.

RCs for a_w calculation of the cookie samples during storage are shown in Table S3 in Supplementary material. The regression analysis revealed that RCs involved in the a_w calculation, associated with the linear term of t and the nonlinear term of $t \times T$, were statistically significant ($p<0.01$).

In the cases where interaction between factors was statistically significant, complete information regarding the effect of the factors on the responses can be perceived on the basis of the three-dimensional contour plots. The plot of the a_w (Fig. 2a) values was superimposed to show the dependence of temperature (T), storage time (t) and packaging condition (P=0 – unpacked cookies; P=1 – packed cookies). The observed three-dimensional contour plot of a_w surface showed a 'rising ridge' pattern, with the augment in the a_w value as storage time (t) increased and as the temperature (T) decreased (Fig. 2a).

Figure 2. Three-dimensional contour plot of a_w, F and HMF responses, affected by temperature (T), storage time (t), and packaging condition (P=0 – unpacked cookies; P=1– packed cookies)

3. 2. 2. Effects of storage condition on peak force (F)

Storage stability was further considered through physical characteristic associated with the peak force (F) at the time of interruption (the point of break) (Table S1). According to Giannou, et al.

(2014), dry food systems such as cookies can lose their desired textural properties during storage or upon the opening of the package. Also known hypothesis that sucrose recrystallization in cookies that are high in sugar and low moisture is responsible in part for the firming of soft cookies was demonstrated by Belcourt and Labuza (2007). Prolonged exposure of these products to ambient storage conditions leads to water absorption from the atmosphere into the product's matrix, changing the textural properties. Moreover, firmness was influenced by temperature, which promoted water migration from the core of the cookies of a lower a_w content, resulting in a stiffer and harder texture product, Farris and Piergiovanni (2009). The maximum peak force of the unpacked cookies kept at ambient temperature (23 ± 1 °C), in fact, had very different values during storage, as it increased in two months (Table S1), while it did not increase at all, quite on the contrary the values decreased, until the third month storage, with the exception of the last two inspection months. The F values were different between the two cookie lots, kept at an elevated temperature (40 ± 1 °C). It should be pointed out that the packed samples became harder. This may be due to a progressive migration of water from the surface to the inside of the cookies, leading to a structural change in the inner part of the samples. Cookies packaged in OPP/OPP – polypropylene/polypropylene bags, at elevated temperature, probably underwent water redistribution, with consequent changes in the cookie firmness, Giannou et al., 2014.

RCs for the model that describes the changes of F during storage are presented in Table S3. It is easily seen from the values, that there was a significant influence of the quadratic term of T, and the interchange terms t × T and T × P.

From the data in Figure 2b, two 'hillside' surfaces were formed in the F contour plot. The first surface of the F values was formed with an increase in storage time (for P=1), and the second surface was formed with the decrease in temperature (for P=0).

3. 2. 3. Effects of storage condition on HMF content

Regarding the interaction effects of storage conditions, it can be noticed that they also had the significant effects ($p < 0.05$) on the HMF content of the cookies (Table S1). The content of HMF detectable in foods is directly related to the heat applied during processing or storage of carbohydrate-rich products. As the temperature and time values increased, the HMF content was mainly observed to increase. Apart from temperature and storage time, the rate of HMF formation in foods is dependent on the type of sugar, pH, water activity, and the concentration of divalent cations of the media, Fogliano, 2014. The most interesting aspect of this is the fact that it has been proposed that HMF formation in foods can have different pathways and an alternative pathway to the HMF formation from sucrose, Perez-Locas and Yaylayan, 2008. In some previous studies (Toker, et al., 2013), the effects of some processing variables on the content of HMF were individually investigated. However, the possible effects of processing or storage factors should be simultaneously studied in combination with each other. The results from this study indicated the minimum HMF content generated from the packed cookie samples kept at ambient temperature. Based on the obtained results, it can be recommended that the cookie samples should be kept packed under low temperatures within short storage times in order to limit the rate of HMF formation content in such products.

From the signs of the regression coefficients presented in Table S3, it can be seen that a further increase in the temperature values could lead to an increase in the HMF contents of the cookie samples, as can also be seen by the nonlinear terms of $t \times T$, and $t \times P$, statistically significant at $p<0.01$ level, and the quadratic term of t and the nonlinear term $T\times P$, statistically significant at $p<0.05$ level.

The counter plot response of HMF also showed a 'rising ridge' configuration, with the higher values of HMF as temperature (t) and storage time (t) increased (Fig. 2c).

3. 2. 4. Effects of storage condition on colour parameters

Browning of different kinds of cookies is attributable to non-enzymatic browning reactions, influenced by many variables such as sugar type, a_w values, temperature, pH and overall processing conditions, Secchi, et al., 2011. Moreover, as colour development occurs largely during later stages of storage, it can be used to predict the completion of shelf life. The parameters L*, a*, b*, C*, h, and ΔE* for the top and bottom surface of the cookies are shown in Table S2 in Supplementary material. As far as the effects of storage conditions on the colour properties were concerned, there was no the distinct significant effect on all observed colour properties of the cookie samples, except for the total colour differences ΔE* ($p < 0.05$). The reference taken in each case was the colour of the control cookie (day 0). The value of ΔE* (Table S2) increased as the time of storage increased in the packaged and unpackaged cookies, at both temperature storage. For prolonged storage time, for both temperature and the observed cookies surface (bottom and top), the colour differences were appreciative by the human eye (well perceived (ΔE* = (3 – 6)) or obvious variations of colour (ΔE* > 6)).

In addition, the RCs for the colour parameters calculation are presented in Table S4, in Supplementary material. It could be seen that RCs involved in L* calculation, associated with the linear term of P0 and the nonlinear term of T × P, were statistically significant at $p<0.01$ level. RCs associated with the linear terms of t and P0, included in the prediction of a*, were statistically significant at $p<0.01$ level, while RCs connected to the linear terms of T and P, as well as their nonlinear combination T × P, were significant at $p<0.05$ level. The nonlinear term T

× P, involved in SOP model for b* prediction, was significant at $p<0.01$ level, and the linear term of P0 was statistically significant at $p<0.05$ level. The nonlinear term T × P, used for C* calculation, was statistically significant at $p<0.01$ level, while the linear term of P was significant at $p<0.05$ level. RC connected to the linear term of P0 was statistically significant at $p<0.01$ level in h* calculation, while RCs associated with the linear term of t and the nonlinear terms of t × T and t × P were statistically significant at $p<0.05$ level. RCs associated with the linear term of P0 and the nonlinear term of t × P0 were also statistically significant at $p<0.01$ level.

As with previously observed results, three-dimensional contour plots of L*, a*, b*, h*, C*, and ΔE* colour characteristics were superimposed to show the dependence of temperature (T), storage time (t), packaging condition (P=0 – unpacked cookies; P=1– packed cookies), and the position of the cookie sample (bottom (P0=0) and top (P0=1) surface) (Fig. 3).

The obtained L* surface for P0=0 or P0=1, and P=0 showed a 'rising ridge' pattern, with the augment in L* value as storage time (t) increased (Fig. 3a).

Figure 3. Three-dimensional contour plot of all colour responses, affected by temperature (T), storage time (t), packaging condition (P=0 – unpacked cookies; P=1– packed cookies), and position of cookie sample (Po) (bottom (Po=0) and top (Po=1) surface)

Considering the countour plot L* in the case of P0=0 and P=1 conditions, it could be noticed that the gained L* surface formed a 'saddle point', with the increase in L* value as storage time (t) increased and temperature (T) decreased. Simultaneously, the L* response of P0=1 and P=1 showed a 'rising ridge' configuration, with the rise in L* value as the temperature (T) increased (Fig. 3a).

In respect of the a* response, its count plot indicated a 'hillside' pattern, with the reduction in the a* value as storage time (t) increased. Regarding b* parameter, the calculated b* surface for the P0=0 and P=0 conditions expressed a 'stationary ridge' pattern, with the augment in b* value as storage time (t) increased (Fig. 3c). In the case of the Po=0 and P=1 alternatives, the gained b* surface formed a 'saddle point', with the rise of b* value as storage time (t) increased and temperature (T) decreased. In respect to the b* surface for the Po=1 and P=0 conditions a 'rising ridge' pattern was obtained, with the augment in the b* value as storage time (t) increased and temperature (T) decreased. Additionally, b* response for the Po=1 and P=1 conditions reproduced a 'stationary ridge' configuration, with the rise in the b* value as the temperature (T) increased (Fig. 3c).

It was noticed that the obtained C* surface for the Po=0 and P=0 variations showed a 'saddle point' pattern, with the increase in b* value as storage time (t) increased. In the case of the P0=0 and P=1 conditions, the gained C* surface formed a 'saddle point' configuration, with the increasing C* value as storage time (t) increased and temperature (T) decreased. The obtained C* surface for the Po=1 and P=0 alternatives displayed a 'rising ridge' pattern, with the augment in the C* value as storage time (t) decreased and temperature (T) increased. The C* surface for the Po=1 and P=1 modifications presented a 'hillside' configuration, with the rise in C* value as the temperature (T) increased and storage time (t) decreased (Fig. 3d).

In the case of calculated h* surface for the Po=0 and P=0 conditions, a 'hillside' pattern occurred, with the augment in the h* value as storage time (t) increased. In regard to the Po=0 and P=1 alternatives, the obtained h* surface formed a 'saddle point', with the increase in the h* value as storage time (t) and temperature (T) increased. The accomplished h* surface for the Po=1 and P=0 modifications showed a 'rising ridge' pattern, with the augment in the h* value as storage time (t) increased. At the same time, the h* response to the Po=1 and P=1 conditions expressed a 'stationary ridge' pattern, with the rise in the h* value as temperature (T) and storage time (t) increased (Fig. 3e).

3. 3. Residual analysis of the modelling

Much useful data can be obtained using the statistical analysis of the residuals of the modelling. Oscar, et al. (2002), reported that this analysis could show whether there are any larger differences in any particular area of the model or whether the scatter is random. Because of the above mentioned facts, the residual analysis of the developed models was also performed. Skewness measures the deviation of the distribution from normal symmetry. If skewness is clearly different from 0, then the distribution is asymmetrical, while normal distributions are perfectly symmetrical. Kurtosis measures the 'peakedness' of a distribution. If kurtosis is clearly different than 0, then the distribution is either flatter or more peaked than normal; the kurtosis of the normal distribution is 0.

The analysed mean values, standard deviations (SD), and the variance of the residuals are shown in Table S5, in Supplementary material. A significant lack of fit generally showed that the model failed to represent the data in the experimental domain at which points were not included in the regression, Oscar, et al. (2002). All SOP models had an insignificant lack of fit tests, which means that all the models represented the data satisfactorily.

The coefficient of determination, r^2, was defined as the ratio of the explained variation to the total variation and was explained by its magnitude, Oscar, et al. (2002). It is also the proportion of the variability in the response variable, which was accounted for the regression analysis. A high r^2 indicates that the variation was accounted and the data fitted satisfactorily to the proposed

SOP model. High r^2 values for the observed responses are satisfactory, higher than 0.8, except for the colour difference (ΔE*), and show a good fit of the model to the experimental results (Table S5).

4. Conclusions

The obtained relationship between the independent extrinsic factors (temperature, storage time, packaging and cookie surface position) and the dependent responses (targeted physicochemical parameters) of the gluten-free rice-buckwheat cookie samples could be a useful tool to assess and manage their storage stability. Quantification of these relations through mathematical models represents a great benefit for food technologists since it allows making predictions of the physicochemical indicators as the potential markers of cookie stability during storage. The SOP models developed to investigate the effect of temperature (T), storage time (t), packaging (P) and cookie surface position (Po) on the observed physicochemical parameters, showed a good fit to the experimental data with $r^2>0.8$ for a_w, HMF, F, L*, a*, b*, C*, and h*. This led to the conclusion that within the range of the observed parameters in this study, the most convenient HMF values were gained when a low storage temperature regime was applied. However, the a_w value decreased in the packed gluten-free rice-buckwheat cookie samples. The augment of F was noticed by an increase of storage time (t), regardless of the packaging of the gluten-free rice-buckwheat cookie samples. The L*, b*, C*, h*, and ΔE* values decreased over time, while the a* value increased in the unpacked samples during the storage time. In general, the developed empirical models gave a reasonable fit to experimental data and predicted the targeted physicochemical properties at a satisfactory level, and could be successfully implemented to cookies stability process control.

Funding

This work was financially supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Project No. TR31029).

References

Ariffin, A. A., Ghazali, H. M., Kavousi, P. 2014. Validation of a HPLC method for determination of hydroxymethylfurfural in crude palm oil. Food Chem. 154, 102–107.

Baixauli, R., Salvador, A., Fiszman, S. M. 2008. Textural and colour changes during storage and sensory shelf life of muffins containing resistant starch. Eur. Food Res. Technol. 226, 523–530.

Belcourt, L., Labuza, T. 2007. Effect of raffinose on sucrose recrystallization and textural changes in soft cookies. J. Food Sci. 72, 65–71.

Blackburn. C, de W. 2000. Modeling shelf-life. In The stability and shelf-life of food; Kilcast, D.; Subramaniam, P., Eds.; Woodhead Publishing Ltd: Abington Hall, Bington, Cambridge, UK, pp. 55–75.

Cauvain, S.P., Young, L.Y. 2008. Bakery Food Manufacture and Quality: Water Control and Effects. Press: John Wiley & Sons, Ltd., Publication, UK, pp. 174–198.

Dapčević Hadnađev, T., Torbica, A., Hadnađev, M. 2013. Influence of buckwheat flour and carboxymethyl cellulose on rheological behaviour and baking performance of gluten-free cookie dough. Food Bioprocess Tech. 6, 1770–1781.

da Silva, T.F., Conti-Silva, A.C. 2016. Preference mappings for gluten-free chocolate cookies: Sensory and physical characteristics. Nutrition & Food Science, 46, 374–387.

Farris, S., Piergiovanni, L. 2009. Optimization of manufacture of almond paste cookies using response surface methodology. J. Food Process Eng. 32, 64–87.

Fogliano, V. 2014. Maillard reaction products: occurrence, mitigation strategies and their physiological relevance. Doctoral Thesis, Corvinus University of Budapest, Faculty of Food Science, Department of Food Chemistry and Nutrition, Budapest.

Jacob, J., Leelavathi, K. 2007. Effect of fat-type on cookie dough and cookie quality. J. Food Eng. 79, 299–305.

Giannou,V., Lebesi, D., Tzia, C. 2014. Packaging and Shelf-life Prediction of Bakery Products. In Bakery Products Science and Technology; Zhou, W.; Hui, Y. H.; De Leyn, I.; Pagani, M. A.; Rosell, C. M.; Selman, J. D.; Therdthai, N., Eds., John Wiley & Sons, Ltd., UK, pp. 354–371.

- - - Villanova, B. 2010. Determination of furan precursors and some thermal damage markers in baby foods: ascorbic acid, dehydroascorbic acid, hydroxymethylfurfural and furfural. J. Agr. Food Chem. 58, 6027–6032.

Moore, D., McCabe, G. 2003. Introduction to the Practice of Statistics. Press: W.H. Freeman and Co., New York, pp. 438. ISBN 9780716796572.

Oscar, T. P. 2002. Development and validation of a tertiary simulation model for predicting the potential growth of Salmonella typhimurium on cooked chicken. Int. J. Food Microbiol. 76, 177–190.

Perez-Locas, C., Yaylayan, V.A. 2008. Isotope labeling studies on the formation of 5-(hydroxymethyl)-2-furaldehyde (HMF) from sucrose by pyrolysis-GC/MS. J. Agr. Food Chem. 56, 6717–6723.

Pérez, S., Matta, E., Osella, C., de la Torre, M., Sánchez, H.D. 2013. Effect of soy flour and whey protein concentrate on cookie colour, LWT - Food Sci. Technol. 50, 120–125.

Petisca, C., Henriques, A. R., Pérez-Palacios, T., Pinho, O., Ferreira, I. M. P. L. V. O. 2014. Assessment of hydroxymethylfurfural and furfural in commercial bakery products. J. Food Compos. Anal. 33, 20–25.

Pestorić, M., Šimurina, O., Filipčev, B., Jambrec, D., Belović, M., Mišan, A., Nedeljković, N. 2015. Relationship of physicochemical characteristics with sensory profile of cookies enriched with medicinal herbs. Int. J. Food Prop. 18, 2699–2712.

Rosell, C.M., Raquel Garzon, R. 2015. Chemical Composition of Bakery Products. In Handbook of Food Chemistry; Cheung, P.C.K.; Mehta, B.M., Eds.; Springer-Verlag: Berlin Heidelberg, pp. 192–222.

Rufián-Henares, J. A., Andrade, C. D., Morales, F. J. 2006. Application of a fast high-performance liquid chromatography method for simultaneous determination of furanic compounds and glucosylisomaltol in breakfast cereals. J. AOAC Int. 89, 161–165.

Sakač, M., Pestorić, M., Misan, A., Nedeljković, N., Jambrec, D., Jovanov, P., Banjac, V., Torbica, A., Hadnđev, M., Mandić, A. 2015. Antioxidant capacity, mineral content and sensory properties of gluten-free rice and buckwheat cookies. Food Technol. Biotech. 53, 38–47.

Sakač, M., Pestorić, M., Mandić, A., Mišan, A., Nedeljković, N., Jambrec, D., Jovanov, P., Lazić, V., Pezo, L., Sedej, I. 2016. Shelf-life prediction of gluten-free rice-buckwheat cookies. J. Cereal Sci. 69, 336–343.

Secchi, N., Stara, G., Anedda, R., Campus, M., Piga, A., Roggio, T., Catzeddu, P. 2011. Effectiveness of sweet ovine whey powder in increasing the shelf life of 'Amaretti' cookies. LWT - Food Sci. Technol. 44, 1073–1078.

Schläpfer, K. 2002. Farbmetrik in der grafischenIndustrie. UGRA: St. Gallen, , ISBN 3-9520403-1–2.

Toker, O.S., Dogan, M., Ersöz, N.B., Yilmaz, M.T. 2013. Optimization of the content of 5-hydroxymethylfurfural (HMF) formed in some molasses types: HPLC-DAD analysis to determine effect of different storage time and temperature levels. Ind. Crop. Prod. 50, 137–144.

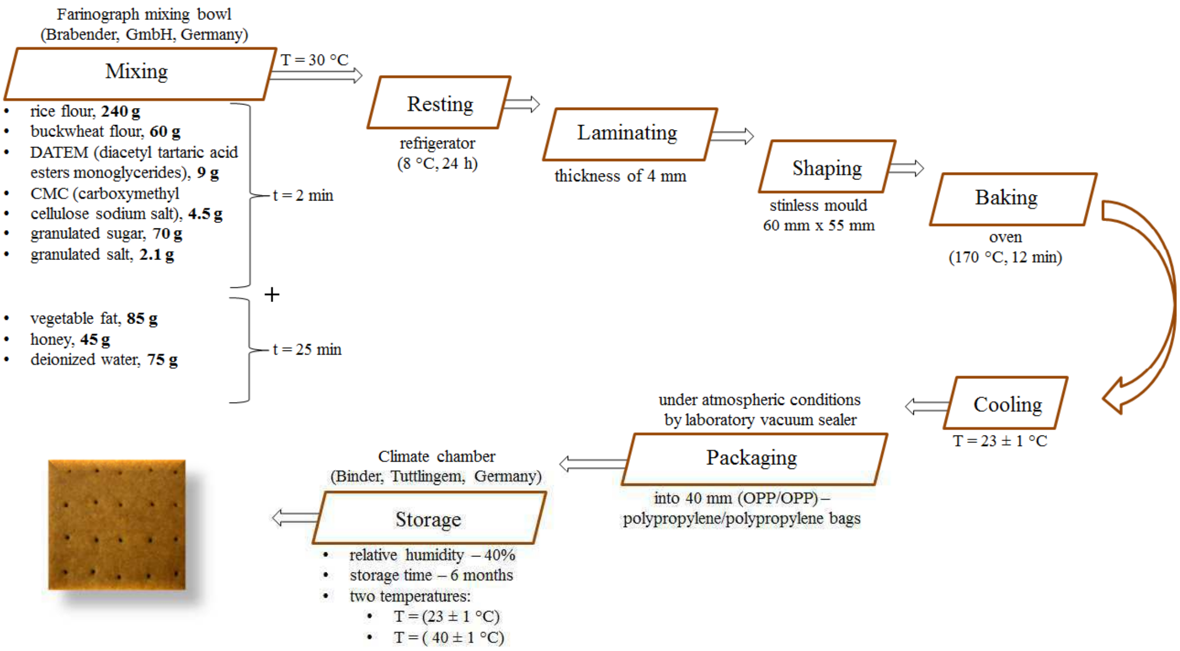
Turan, D., Capanoglu, E., Altay, F. 2015. Investigating the effect of roasting on functional properties of defatted hazelnut flour by response surface methodology (RSM). LWT - Food Sci. Technol. 63, 758–765.

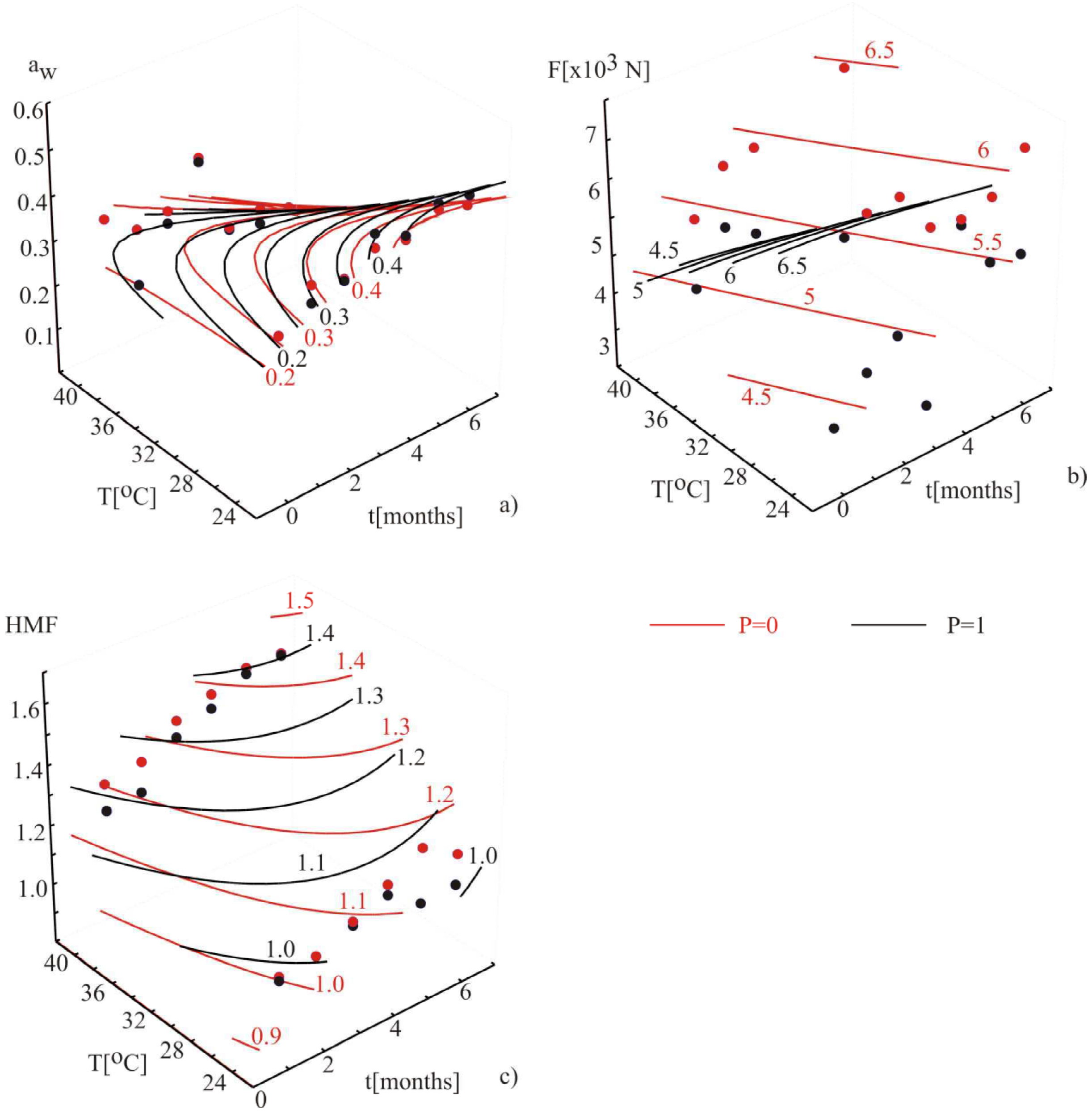
Torbica, A., Hadnađev, M., Dapčević, T. 2010. Rheological, textural and sensory properties of gluten-free bread formulations based on rice and buckwheat flour. Food Hydrocolloids, 24, 626–632.

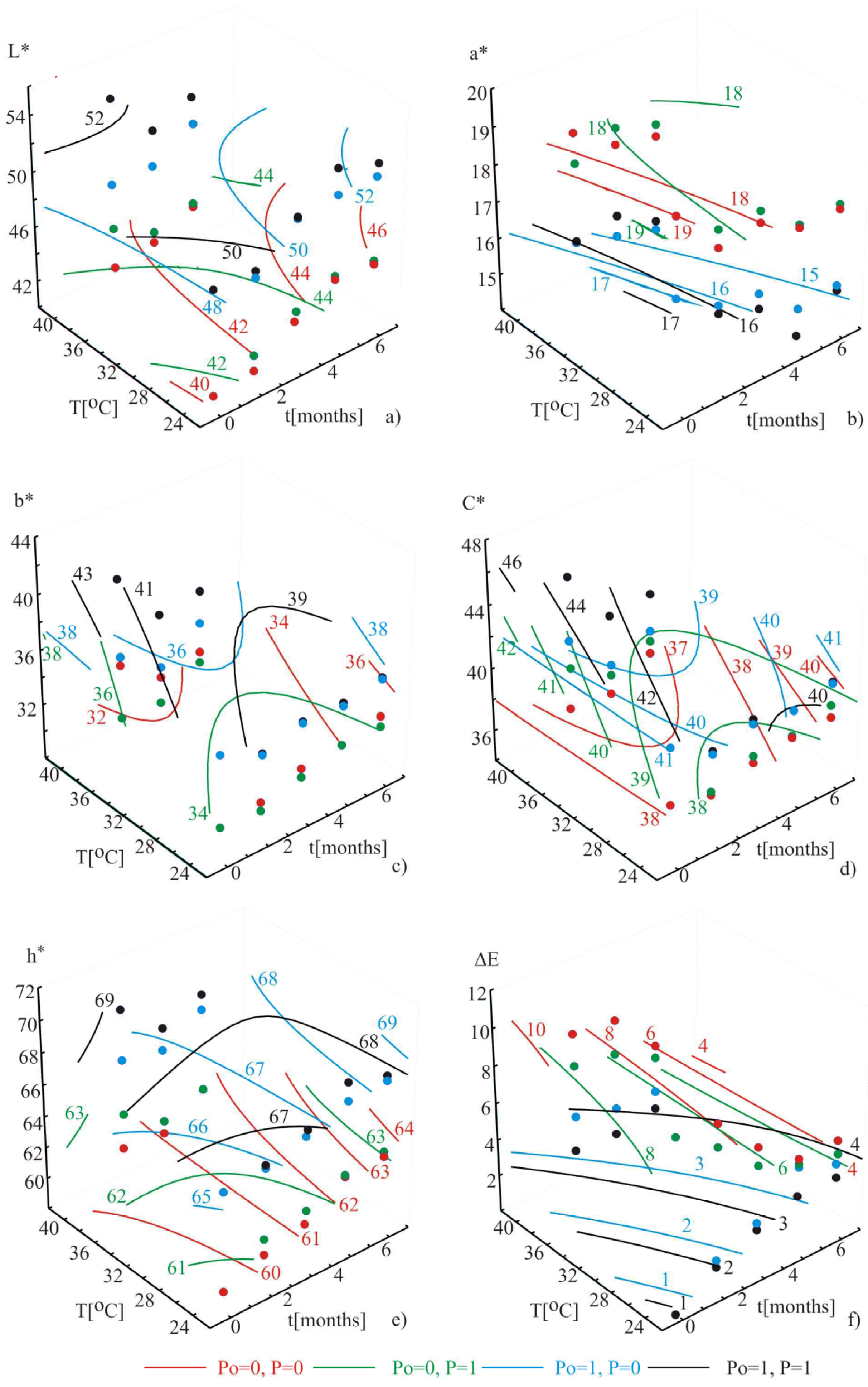
van Der Fels-Klerx, H.J., Capuano, E., Nguyena, H.T., AtaçMogol, B., Kocadağlı, T., GöncüoğluTaş, N., Hamzalıoğlu, A., Van Boekel, M.A.J.S., Gökmenb, V. 2014. Acrylamide and 5-hydroxymethylfurfural formation during baking of biscuits: NaCl and temperature–time profile effects and kinetics. Food Res. Int. 57, 210–217.

Wibowo, S., Grauwet, T., Gedefa, G.B., Hendrickx, M., van Loey, A. 2015. Quality changes of pasteurised mango juice during storage. Part I: Selecting shelf-life markers by integration of a targeted and untargeted multivariate approach, Food Res. Int. 78, 396–409.

Yang, N., Hort, J., Linforth, R., Brown, K., Walsh, S., Fisk, I.D. 2013. Impact of flavor solvent (propylene glycol or triacetin) on vanillin, 5-(hydroxymethyl)furfural, 2,4-decadienal, 2,4-heptadienal, structural parameters and sensory perception of shortcake biscuits over accelerated shelf life testing. Food Chem. 141, 1354–1360.


Farinograph mixing bowl
(Brabender, GmbH, Germany)
Mixing
T = 30 °C
rice flour, 240 g
buckwheat flour, 60 g
DATEM (diacetyl tartaric acid esters monoglycerides), 9 g
CMC (carboxymethyl cellulose sodium salt), 4.5 g
granulated sugar, 70 g
granulated salt, 2.1 g
t = 2 min
+
vegetable fat, 85 g
honey, 45 g
deionized water, 75 g
t = 25 min
Resting
refrigerator
(8 °C, 24 h)
Laminating
thickness of 4 mm
Shaping
stinless mould
60 mm x 55 mm
Baking
oven
(170 °C, 12 min)
Cooling
T = 23 ± 1 °C
under atmospheric conditions
by laboratory vacuum sealer
Packaging
into 40 mm (OPP/OPP) – polypropylene/polypropylene bags
Climate chamber
(Binder, Tuttlingem, Germany)
Storage
relative humidity – 40%
storage time – 6 months
two temperatures:
T = (23 ± 1 °C)
T = (40 ± 1 °C)


a_w
0.6
0.5
0.4
0.3
0.2
0.1
0.4
0.4
0.3
0.3
0.2
0.2
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
a)
F[x10^3 N]
7
6
5
4
3
6.5
6
5.5
5
4.5
4.5
5
6
6.5
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
b)
HMF
1.6
1.4
1.2
1.0
1.5
1.4
1.4
1.3
1.3
1.2
1.2
1.1
1.1
1.0
1.0
1.0
0.9
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
c)
P=0
P=1


L*
54
50
46
42
52
44
52
46
50
50
44
44
48
42
42
40
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
a)
a*
20
19
18
17
16
15
18
18
18
19
19
17
16
15
17
16
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
b)
b*
44
40
36
32
43
41
39
34
38
36
38
38
36
36
32
34
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
c)
C*
48
44
40
36
46
44
39
40
41
42
37
38
39
40
41
42
40
40
41
40
39
38
38
40
36
32
28
24
0
2
4
6
t[months]
d)
h*
72
70
68
66
64
62
60
69
68
69
68
67
63
66
67
64
63
63
62
62
65
61
61
60
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
e)
ΔE
12
10
8
6
4
2
10
8
6
4
8
3
6
4
4
3
2
2
1
1
40
36
32
28
24
T[°C]
0
2
4
6
t[months]
f)
Po=0, P=0
Po=0, P=1
Po=1, P=0
Po=1, P=1