

OPTIMIZATION OF A LIQUID IMPROVER FOR BARBARI BREAD: STALING KINETICS AND RELATIONSHIP OF TEXTURE WITH DOUGH RHEOLOGY AND IMAGE CHARACTERISTICS

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ABSTRACT

The effect of liquid improver components on texture of Barbari flat bread was examined. Glycerol, sodium stearyl-2-lactylate (SSL) and enzyme-active soy flour (ESF) were evaluated as improver constituents. Texture characteristics were further correlated with dough rheology, quality, image features and shelf life of bread. Statistical analysis suggests that more than 50% of the whole structural variance existing between bread samples could be interpreted by texture parameters. The optimum improver combination was found to be 1.27% of glycerol, 0.41% of SSL and 1.59% of ESF when desirable function method was applied. The variations of hardening rates with time were used to test 11 different models. In studying the consistency of each model, some statistical tests, such as reduced χ^2 , mean bias error and root mean square error were also used as well as correlation coefficients. The results of these tests have also confirmed the consistency of the Rational model.

PRACTICAL APPLICATION

This methodology simplifies the study of bread textural parameters during storage and the result interpretation. The correlation analysis has demonstrated that the number of textural parameters of breads to study can be reduced.

INTRODUCTION

Flat breads are the main dietary staple in many Middle Eastern and North African countries. In today's demanding world, the use of bread improvers has become an indispensable part of enhancing the quality of bakery products. Bread improvers are technically sophisticated blends of functional ingredients, which if formulated correctly, will enhance the development of dough structure, facilitate trouble-free production and provide the desired result of consistent products having optimal quality at the lowest possible cost (Ghorbel *et al.* 2010). There are several disadvantages related to the use and handling of solid bread improver compositions. Handling problems occur in medium- and large-size industrial bakeries. These bakeries would like to employ automatic dosing systems for ingredients such as bread improving compositions and yeast. However, solid bread improver compo-

sitions are difficult to be pumped and dosed automatically in comparison with the liquid types. Furthermore, such solid compositions make cleaning of the bread making machinery harder in comparison with the liquid improvers (Cabrera and Heeren 1997).

The study of bread staling is of interest in both scientific and commercial points of view. Scientifically, in spite of the considerable work done in this field, a large number of unanswered questions still exist; whereas commercially, bread staling is responsible for significant financial loss to both consumer and bread producer (Russell 1983). Staling involves the hardening of the crumb that is a complex phenomenon in which multiple mechanisms operate. Factors affecting wheat bread crumb staling have been extensively investigated (Zobel and Kulp 1996; Schiraldi and Fessas 2000). Although the main factor involved is considered to be starch retrogradation, many studies have shown that starch

retrogradation is not the only factor responsible for crumb staling (Baik and Chinachoti 2001). When the retrogradation of amylopectin occurs, water molecules are incorporated into the crystallites and the distribution of water is shifted from gluten to starch/amylopectin, thereby changing the nature of the gluten network (Gray and Bemiller 2003). Besides the molecular order of starch, water also plays an important role in crumb firmness because of its plasticizing effect on the crumb network (Hug-Iten *et al.* 2003). Starch retrogradation involves reassociation of starch component molecules into a partially crystalline, ordered structure. Amylopectin recrystallization requires several days. Because firming of bread also develops over several days, most staling models view the changes in amylopectin as the primary cause for crumb firming (Zobel and Kulp 1996). Use of non-linear regression models appears to be the most useful tool for crumb firming studies when discontinuities with time are not considered (Mälkki *et al.* 1978). In this analysis, specific irregular data are corrected using the remaining values and accurate estimation of kinetic parameters is performed.

Among the functional food additives, polyols have been increasingly used to improve the quality and shelf life of bread. Gliemmo *et al.* (2006) showed that using polyols can depress the water activity and improve texture and mouthfeel. Glycerol (Gly) as a polyol has been used successfully to extend the shelf life of meal ready to eat bread used by the military (Hallberg and Chinachoti 1992), Barbari bread fortified with soy flour (Pourfarzad *et al.* 2011), as well as flour tortillas (Suhendro *et al.* 1995). Emulsifiers, a subset of surfactants, have been widely used by the baking industry. The function of surfactants, as crumb-softening agents, is closely related to their interaction or complex formation with starch, particularly the linear amylose fraction, to retard bread staling. Emulsifiers may also slow the rate of bread firming by forming a complex with the amylopectin fraction within the starch granule (Kamel and Ponte 1993). Sodium stearyl-2-lactylate (SSL) is one of the most efficient surfactants in breadmaking. The improvement in bread quality and rheological characteristics of dough with SSL was reported by several researchers (Gomez *et al.* 2004; Azizi and Rao 2005a,b). Soybean-derived products such as enzyme-active soy flour (ESF) are among the ingredients often considered as suitable supplements in food products, such as bread, because of their known health-promoting activity (Godfrey and Limpert 2002) and staling-reducing effect (Zhang 2004). A literature survey indicated that no work has been carried out on the effect of a liquid bread improver containing emulsifier, polyol, ESF and water on the quality, shelf life and sensory characteristics of bread. Thus, it is expected that an improver containing all of these ingredients will be more effective. Also, up to now, in most of the bread staling studies, bread features were fitted to the Avrami equation and to the best of our knowledge, there is no any pub-

lished work that models these characteristics to other mathematical models. Thus, the present study was designed: (1) to examine the effects of Gly, SSL and ESF on Barbari flat bread texture during storage when used alone as well as in combination at different levels; (2) to determine the optimum formulations for Barbari flat bread improver; (3) to check the validity of response surface methodology to analyze the additive, synergistic and/or antagonistic effects of improver components on the quality, shelf life, image and sensory properties; (4) to obtain their relation with dough rheology, quality and image parameters as a way to propose simple procedures to quantify texture that could have an effect on bread shelf life; and (5) to search the possibility of expressing the bread hardening with the different mathematical models by investigating the staling behavior.

MATERIALS AND METHODS

Materials

Commercial *Triticum aestivum* wheat flour (locally named Setareh) was procured from the AceeArd Co., Khorasan, Iran. Dried active yeast was obtained from Fariman Co., Khorasan, Iran. Glycerol (Gly) was purchased from J.T. Baker Chemical Company (Phillipsburg, NJ). SSL was provided by Vista Tejarat Company (Tehran, Iran). ESF was obtained from Toos Soya Co., Khorasan, Iran.

Methods

Chemical and Physical Analysis of Flours. Moisture (44–15.02), ash (08–07), fat (30–10), wet gluten (38–11) and falling number (56–81) were determined according to official standard methods (AACC 2000). The flour's protein was tested using a Kjeltac auto protein tester (model 1030, Tecator Co., Hoeganaes, Sweden). Three replications were taken for each characteristic.

Box–Behnken Design

Table 1 shows the generated Box–Behnken design of three factors (liquid improver components) and three levels using the software Design Expert Version 6.0.10 (Stat-Ease Corporation, Minneapolis, MN). The design consists of 15 sets of test conditions where three levels were attributed to each factor at high, central and low levels, with additional three replicated center points. Maximum and minimum ingredient levels were chosen by carrying out preliminary screening tests and according to the literature reports and economic aspects.

Preparation of Liquid Improvers. Liquid improvers were prepared using glycerol, SSL, ESF and water in the ratio

TABLE 1. VARIABLES AND LEVELS USED IN BOX-BEHNKEN DESIGN FOR LIQUID IMPROVER PRODUCTION

Trial	Variable codes			Actual values		
	Gly	SSL	ESF	Gly (g/100 g)	SSL (g/100 g)	ESF (g/100 g)
1	-1	-1	0	0.00	0.00	1.00
2	1	-1	0	4.00	0.00	1.00
3	-1	1	0	0.00	0.50	1.00
4	1	1	0	4.00	0.50	1.00
5	-1	0	-1	0.00	0.25	0.00
6	1	0	-1	4.00	0.25	0.00
7	-1	0	1	0.00	0.25	2.00
8	1	0	1	4.00	0.25	2.00
9	0	-1	-1	2.00	0.00	0.00
10	0	1	-1	2.00	0.50	0.00
11	0	-1	1	2.00	0.00	2.00
12	0	1	1	2.00	0.50	2.00
13	0	0	0	2.00	0.25	1.00
14	0	0	0	2.00	0.25	1.00
15	0	0	0	2.00	0.25	1.00

Gly, glycerol; SSL, sodium stearoyl-2-lactylate; ESF, enzyme-active soy flour.

of 1:1:1:4 and according to Table 1. Results of preliminary trials indicated this ratio yield proper viscosity of improver for handling and functional properties of bread. First, dispersions were made, and then the dispersions, under continuous agitation, were heated to 50°C. Improvers were prepared by cooling at 4°C.

Rheological Properties of Dough. The effect of the different combinations (15 treatments) of improver ingredients on dough rheology during mixing was examined with the Farinograph (Brabender, Duisburg, Germany) following official standard method 54-21.01 (AACC 2000). The parameters determined were: water absorption, arrival time, dough-development time, stability, mixing tolerance index and dough degree of softening at 20 min. The prepared dough in the Farinograph was cut into two parts of 150 g each and passed through the balling and molding unit of the Extensograph (Brabender, Duisburg, Germany). After 45-min resting in the fermentation cabinet, the dough was stretched. The same procedure was repeated for three times, following the standard method 54-10.01 (AACC 2000). Rheological parameters, namely extensibility (E), resistance to extension (R) and R/E were evaluated in an extensogram. The gelatination temperature was determined with the Amylograph (Brabender, Duisburg, Germany) according to standard manner 22-10.01 (AACC 2000).

Bread Making and Evaluation. The bread formula used for this kind of bread consisted of flour (100 parts); compressed yeast (2 parts); salt (2 parts); sugar (1 part); short-

ening (1 part); and water (based on water absorption at 400 BU). This consistency was found by experimentation to give the most reliable prediction of baking absorption (Maleki *et al.* 1981) when mixed with the dry ingredients at different speeds. Liquid improvers were mixed in the mixer (Electronic Stand Mixer, Hugel, Neuss, Germany) for 10 ± 1 min at 100 rpm with other ingredients of bread formula. Batch size for each treatment was 2 kg. A baking technique, similar in principle to that of commercial procedures, was used for baking experimental loaves ($15 \times 25 \times 2.5$ cm) having almost equal volumes. The ingredients were mixed to optimum dough development. The dough samples were fermented in sealed containers at $30 \pm 5^\circ\text{C}$ and 75–85% relative humidity for 60 ± 5 min, and then divided into 200 ± 1 -g pieces and rounded by hand. The pieces were allowed to proof for 10 ± 1 min in a sealed container placed in the proofing cabinet of oven (Minicombo rotor oven, Zucchelli, Trevenzuolo, Italy). The proofed dough pieces were passed through two pairs of sheeting rolls (gap of 2 mm). The oval-shaped dough pieces were then punched with a special hand puncher, which inserted rectangular (1×2 mm) holes into the sheeted dough. The dough pieces were then baked in a laboratory air impingement oven for 13 ± 1 min at $260 \pm 5^\circ\text{C}$ to obtain the proper thickness and acceptable color and texture. After cooling, bread samples were packed in polyethylene bags, stored at room temperature and evaluated.

Quality analysis of fresh bread samples was carried out by measuring moisture content and specific volume of the central slice (rapeseed displacement). Moisture content was determined according to AACC (2000) standard method 44-15.02. To determine specific volume, slices of 10×10 mm were cut from the center of the bread samples using a metal template (Pourfarzad *et al.* 2011).

Sensory Evaluation. Sensory analysis was performed by 10 trained panelists. The bread quality was investigated using the Iranian flat bread evaluation method described by Rajabzadeh (1991). The overall quality of bread was evaluated by considering the quality characteristics such as bread shape, crust, upper and beneath surface, cavity and porosity, firmness and softness of texture, chewing ability, taste and aroma.

Image Analysis. For each bread loaf, three slices were obtained from the cross and longitudinal sections of central region and images were captured using a flatbed HP Scanjet G4010 Photo Scanner (Hewlett-Packard, Palo-Alto, CA) supporting Desk Scan II software (Hewlett-Packard). A single 60×60 -mm square field of view was evaluated for each image. Brightness was adjusted to 150 units and contrast to 170 units. Images were scanned full scale in 256 grey levels at 150 dots per inch (dpi) each comprising 355 columns by

355 rows of picture elements (pixels) (Crowley *et al.* 2002). JPEG image file format were analyzed with ImageJ 1.4 g (National Institute of Health, Bethesda, MD).

The CIE $L^*a^*b^*$ (or CIELAB) color model was used for determination of the crumb and crust color. The three parameters of such model represent the lightness of color (L^*), which ranges from 0 to 100 (black to white), its position between red and green (a^* , negative values indicate green while positive values indicate red), and its position between yellow and blue (b^* , negative values indicate blue and positive values indicate yellow) (Quevedo *et al.* 2009). Because images were acquired in the red, green and blue color space, space conversion were carried out to obtain CIE $L^*a^*b^*$ model parameters. The average values of L^* , a^* and b^* colors describing the outer crust and inner crumb regions were obtained from all 15 baked samples. The total color difference, ΔE of the bread slices from the reference is:

$$\Delta E = \left[(L_o - L)^2 + (a_o - a)^2 + (b_o - b)^2 \right]^{\frac{1}{2}} \quad (1)$$

where $L_o = 100$, $a_o = 0$ and $b_o = 0$ (Mohd Jusoh *et al.* 2009).

To evaluate crumb structure, color images were converted to 8-bits 256 gray level images. The thresholding method (conversion to a binary image) of the 256 gray-level digital images was used for image segmentation according to Otsu (1979). The selected crumb grain features were the average size, area fraction (cell to total area ratio), solidity (area to convex area) and circularity ($4 \times \pi \times \text{area}/\text{perimeter}^2$) (Angioloni and Collar 2011; Farrera-Rebollo *et al.* 2011). The fractal dimension data were computed using the "Map Fractal Count" plugin of ImageJ software, based on the Minkowski–Bouligand dimension method, also known as box-counting dimension. It systematically lays a series of grids of decreasing box size over the grayscale elevation map and records the number of boxes for each successive grid size, finding the fractal dimension as the slope of the logarithmic regression line for the box numbers and grid sizes (Campos *et al.* 2009). Moreover, cell wall thickness was evaluated using "Euclidian distance map" plugin of ImageJ software based on the coupled analysis of binary and skeletonized (linearized) images.

Texture Analysis. Staling phenomenon and its changes were evaluated by penetration test. A texture analyzer (model QTS 25 kg, CNS Farnell, Hertfordshire, UK) was used to measure the force required for penetration of a round-bottom (2.5 cm diameter \times 1.8 cm height) probe at a velocity of 30 mm/min into the bread samples. The probe descended 30 mm (a sufficient distance to pass through the slice of 10×10 cm of bread) and the trigger force was set at 0.05 N (Pourfarzad *et al.* 2011). The bread samples were evaluated 1 h, 2, 4, 6 and 8 days after baking for shelf life by monitoring the bread hardness.

Statistical Analyses. For each of the response variables, multiple linear regression analysis was used and the data were fitted as linear or quadratic models. From this information, the most accurate model was chosen via the sequential F -tests, lack-of-fit tests and other adequacy measures. In this study, predictor variables were permitted to be at any level within the range of the design. All experiments were carried out in triplicate. Quadratic equation for the variable was as follows:

$$Y : \beta_0 + \sum \beta_{ii} X_i X_i + \sum_i \sum_j \beta_{ij} X_i X_j \quad (2)$$

where Y is the predicted response; β_0 a constant; β_i the linear coefficient; β_{ii} the squared coefficient; and β_{ij} the cross-product coefficient. In addition, lack-of-fit, coefficients of determination (R^2), adj- R^2 , coefficient of variation (CV) and significant probabilities were calculated to check the model adequacy. The quadratic equation shown earlier was used to build surfaces for the variables. The software Design Expert Version 6.0.10 was used to analyze the results. Regression and correlation analyses were conducted using Minitab 15 software (Minitab Inc., State College, PA).

Optimization and Verification Procedures. Besides explaining the behavior of variables by the contour curves, the models fitted in this study could also be utilized for optimization purposes using the desirability function. Optimization was based on generation of the best results for rheology, quality, shelf life, sensory and image properties of Iranian Barbari flat bread. The calculation of the optimal levels of ingredients to be used was performed using a multiple-response method called desirability. This optimization method incorporates desires and priorities for each of the variables.

The rheology, quality, shelf life over 7 days, sensory and image properties of Barbari bread were determined after improver production under optimal formulation. In order to determine the validity of the model, the experimental and predicted values were compared by paired t -test using Minitab 15 software.

Mathematical Modeling of Staling Curves. After improver production under optimal formulation, the staling curves obtained were processed for staling rates to find the most convenient model among different expressions given in Table 6. The hardness ratio was expressed as:

$$HR = \frac{H_\infty - H_t}{H_\infty - H_0} \quad (3)$$

where H_0 is the bread hardness at zero time, H_∞ is the bread hardness at ∞ time, H_t is the bread hardness at t time.

Regression was done using the CurveExpert 1.3 software (Starksville, MS). The correlation coefficient (r) was one of the primary criterions for selecting the best equation to

define the staling curves of breads. In addition to r , the various statistical parameters such as reduced chi-square (χ^2), mean bias error (MBE) and root mean square error (RMSE) were used to determine the quality of the fit. These parameters can be calculated as following:

$$\chi^2 = \frac{\sum_{i=1}^N (HR_{\text{exp},i} - HR_{\text{pre},i})^2}{N - n} \quad (4)$$

$$MBE = \frac{1}{N} \sum_{i=1}^N (HR_{\text{pre},i} - HR_{\text{exp},i}) \quad (5)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (HR_{\text{pre},i} - HR_{\text{exp},i})^2 \right]^{\frac{1}{2}} \quad (6)$$

Where $HR_{\text{exp},i}$ stands for the experimental hardness ratio found in any measurement and $HR_{\text{pre},i}$ is predicted hardness ratio for this measurement. N and n are the number of observations and the number of constants.

RESULTS AND DISCUSSION

Chemical and Rheological Characteristics of Flour Samples

The characteristics of the flour used in this study are in the range of typical values of medium strong flour, suitable for Iranian Barbari flat bread. The flour had $10.52 \pm 0.36\%$ moisture, $10.8 \pm 0.24\%$ protein, $1.76 \pm 0.5\%$ fat, $0.79 \pm 0.006\%$ ash, $26.7 \pm 0.55\%$ wet gluten, $82 \pm 1.5\%$ extraction rate and falling number of 407 ± 3 s.

Response Surface Regression Analysis

The estimated regression coefficients of the quadratic polynomial models for the response variables of texture properties are given in Table 2. Analysis of variance shows that the selected quadratic models adequately represented the data obtained for texture features. The regression models were highly significant for most of texture parameters with satisfactory coefficient of determination (R^2) that varied from 0.515 to 0.973. Moreover, CV describes the extent to which the data were dispersed. The CV (Table 2) for each texture feature was within the acceptable range. Because CV is a measure of expressing standard deviation as a percentage of the mean, the small values of CV give better reproducibility. In general, a high CV indicates that variation in the mean value is high and does not satisfactorily develop an adequate response model (Daniel 1991). The lack-of-fit tests, which measure the fitness of the model, did not result in a significant F value, indicating that the model is sufficiently accurate for predicting the texture characteristics of Barbari bread.

It can be observed that among the three improver components, SSL gave higher effects on texture features. SSL decreased hardness at the first day and during storage. Azizi and Rao (2004) reported a decrease in hardness when SSL gel was added. It was found that glycerol increased hardness of fresh bread but decreased it during storage. Also, positive quadratic effect on hardness at 2, 4 and 6 days were provided by glycerol. Our results showed that ESF had negative linear effect on hardness at 4 and 6 days. On the other hand, positive quadratic effect of ESF was observed on hardness at day 4. The interaction effects also influenced some responses i.e.,

Source	Hardness 0 day (N)	Hardness 2 days (N)	Hardness 4 days (N)	Hardness 6 days (N)	Hardness 8 days (N)
Model	4.135***	8.932***	9.867***	16.593***	16.140***
Gly	1.737*	-0.538*	-0.814**	-6.020**	ns
SSL	-2.925**	-1.683***	-2.516**	-14.204***	-21.451***
ESF	ns		-6.285**	-1.115**	ns
Gly-Gly	ns	0.503*	0.780**	1.679***	ns
SSL-SSL	ns	ns	ns	ns	ns
ESF-ESF	ns	ns	2.290*	ns	ns
Gly-SSL	-5.014**	-3.328*	-5.493**	ns	ns
Gly-ESF	ns	ns	ns	ns	ns
SSL-ESF	ns	ns	ns	ns	ns
Lack of Fit	0.071 ^{ns}	0.650 ^{ns}	0.594 ^{ns}	0.206 ^{ns}	0.304 ^{ns}
C.V.	19.86	14.08	16.90	8.87	17.51
R^2	0.797	0.827	0.918	0.973	0.832
adj R^2	0.741	0.757	0.857	0.962	0.820

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.001$.

CV, coefficient of variation; Gly, glycerol; SSL, sodium stearoyl-2-lactylate; ESF, enzyme-active soy flour; ns, no significant effect at level $<5\%$.

TABLE 2. REGRESSION COEFFICIENTS OF PREDICTED QUADRATIC POLYNOMIAL MODELS FOR TEXTURE PROPERTIES OF BARBARI BREAD

TABLE 3. CORRELATION COEFFICIENTS BETWEEN VALUES OF RHEOLOGICAL CHARACTERISTICS OF DOUGH AND TEXTURE OF BARBARI BREAD

Parameter	Water absorption	Arrival time	Dough development time	Stability	Mixing tolerance index	Degree of softening	Resistance to extension	Extensibility	R/E	Gelatination temperature
H ₀		-0.657**	-0.611*	-0.537*		0.615*	-0.532*			
H ₂				-0.668**	0.636*	0.746**	-0.654**			
H ₄				-0.56*	0.53*	0.679**	-0.56*			
H ₆				-0.749**	0.652**	0.662**	-0.838***		-0.583*	
H ₈				-0.808***	0.818***	0.765**				
H ₀₋₂										
H ₀₋₄								-0.579*		
H ₀₋₆							-0.686**			
H ₀₋₈				-0.613*	0.659**					

* $P < 0.05$.** $P < 0.01$.*** $P < 0.001$.not shown correlation: no significant effect at level < 0.05 . H_t is the bread hardness at t time. H_{0-t} is the bread hardness difference between first day and t time.

hardness at 0, 2 and 4 days, which were negatively influenced by crossed quadratic effect of Gly-SSL. Several researchers investigated the effects of glycerol and ESF on the staling reduction of bread (Tsen and Hoover 1973; Suhendro *et al.* 1995). These works directly reflect the complexity of various changes that modified the bread hardness during storage. This could have contributed to the low predictability of staling. It also shows how critical is a component change in formulation of improver to the quality and staling of the product. Several researchers examined the sensitivity of texture analysis for differentiation of breads according to ingredient (Haros *et al.* 2002; Rosell and Santos 2010). They found that texture analysis was greatly modified in that the firmness of bread was changed by additives.

Interrelationship between Rheological Characteristics of Dough and Texture Characteristics of Bread

Correlation coefficients between various rheological characteristics of dough and texture characteristics of breads are given in Table 3. It is evident from the data that most of the rheological characteristics of dough have significantly affected the texture characteristics of bread. The texture features of the breads were influenced by various rheological parameters. However, among rheological characteristics, stability and degree of softening had the greatest significant coefficients of correlation with texture features. Resistance to extension as an extensographic parameter was found to be negatively correlated to hardness between the first and the sixth days of storage. On the other hand, it was observed that among the texture characteristics, hardness at the first and the sixth days have shown the greatest significant correla-

tions with rheological parameters of dough. No significant correlation was found between water absorption, gelatinization temperature and any of the texture properties. The correlation between bread texture and dough rheology has been reported by many researchers (Armero and Collar 1997; Autio *et al.* 2001).

Interrelationship between Shelf Life, Quality Characteristics and Image Features of Bread

Some of the quality and image characteristics of breads were found to be significantly correlated to shelf life (Table 4). ΔE as an important image parameter, was found to have good correlations with hardness during storage. Breads having a higher ΔE resulted in longer shelf life. It is evident from the data that among quality characteristics of bread, overall quality score was the only parameter that significantly correlated with hardness at the eighth day. Many researchers (Barrett *et al.* 1994; Zghal *et al.* 2002) reported significant correlations between structural characteristics, sensory scores and mechanical characteristics of bakery products. e.g., Kamman (1970) stated that the physical and visual texture of bread crumb are interrelated quality factors that should be considered as a single entity. It was also speculated that crumb physical texture is largely determined by the character of the grain, e.g., cell wall thickness, cell size and uniformity.

Interrelationship between Texture Features of Bread

The interrelationships of texture characteristics are summarized in Table 5. The data revealed positive correlation

TABLE 4. CORRELATION COEFFICIENTS BETWEEN VALUES OF QUALITY, IMAGE AND TEXTURE OF BARBARI BREAD

Parameter	Overall quality score	Moisture content	Specific volume	ΔE	Average size	Fractal dimension	Area fraction	Cell wall thickness	Circularity	Solidity
H ₀					-0.746**		-0.573*			
H ₂				-0.775**	-0.713**					
H ₄				-0.732**	-0.579*					
H ₆				-0.857***	-0.658**					
H ₈	-0.623*			-0.544*	-0.541*					
H ₀₋₂				-0.661**						
H ₀₋₄										
H ₀₋₆										
H ₀₋₈	-0.605*			-0.874***						0.519*

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.001$.

H_t is the bread hardness at t time.

H_{0-t} is the bread hardness difference between first day and t time.

not shown correlation: no significant effect at level <0.05.

between hardness of bread at the first day and during storage. Hardness difference during storage showed positive significant correlation with hardness of each day. The correlation between textural parameters in cakes and white breads has been reported by many researchers (Gómez *et al.* 2008, 2010).

Optimization of Improver Components and Verification of Results

Multiple response optimizations were performed to measure the optimum levels of independent variables to achieve the desired response goals. Specific volume and sensory aspects were desired maximal whereas hardness as an indicator of shelf life was specified as minimum desirable. It is well known that the moisture content of bread crumb is a major contributor to the perception of product freshness and that, within limits, the higher the moisture content, the fresher the bread will be perceived by the consumer. Thus, moisture

content was specified as maximum level desirable. Other parameters were fixed to intermediate level.

The final result for this optimization suggested that a mixture containing 1.27% of Gly, 0.41% of SSL and 1.59% of ESF in liquid improver formulation could be a good mixture of these three improver compounds in order to achieve the best quality, shelf life, sensory and image properties of Barbari bread. This new mixture was submitted to the same experimental procedures applied as those from the beginning of this study (data not shown). There was no significant difference between the estimated and observed values ($P < 0.05$), suggesting a good fit between the models to the experimental data.

Modeling of Staling Curves

Several research workers have attempted to modeling the kinetic of bread staling. Data for intermediate storage time

Parameter	H ₀	H ₂	H ₄	H ₆	H ₈	H ₀₋₂	H ₀₋₄	H ₀₋₆	H ₀₋₈
H ₂	0.704**								
H ₄	0.56*	0.924***							
H ₆	0.571*	0.81***	0.731**						
H ₈		0.601*		0.599*					
H ₀₋₂			0.571*						
H ₀₋₄	0.603*					0.701**			
H ₀₋₆		0.656**	0.654**	0.861***		0.686**			
H ₀₋₈					0.851***				

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.001$.

H_t is the bread hardness at t time.

H_{0-t} is the bread hardness difference between first day and t time.

not shown correlation: no significant effect at level <0.05.

TABLE 5. CORRELATION COEFFICIENTS BETWEEN TEXTURE CHARACTERISTICS OF BARBARI BREAD

TABLE 6. RESULTS OF STATISTICAL ANALYSES ON THE MODELING OF STALING OF BARBARI BREAD AFTER OPTIMIZATION OF LIQUID IMPROVER

Model no.	Name	Model equation	Constants	Correlation coefficient (r)	MBE	RMSE	χ^2
1	Linear	HR = a + bt	a = 0.11032 b = -0.01212	0.958	0	0.0102	1.74×10^{-4}
2	Quadratic	HR = a + bt + ct ²	a = 0.09903 b = -0.00082 c = -0.00141	0.994	2×10^{-13}	0.0039	3.73×10^{-5}
3	Harris	HR = 1/(a + bt ^c)	a = 10.80884 b = 0.00068 c = 5.53195	0.971	2.12×10^{-3}	0.0086	1.85×10^{-4}
4	Rational	HR = (a + bt)/(1 + ct + dt ²)	a = 0.10076 b = -0.0126 c = -0.07002 d = -0.00148	0.998	-1.29×10^{-7}	0.0023	2.65×10^{-5}
5	Newton	HR = exp(-at)	a = 1.15366	0.523	0.1603	0.4033	0.2033
6	Page	HR = exp(-at ^b)	a = 1.91598 b = 0.3042	0.827	0.1805	0.4019	0.2693
7	Logarithmic	HR = a exp(-bt) + c	a = 0.67656 b = 0.01849 c = -0.5661	0.951	1.25×10^{-3}	0.0110	3.05×10^{-4}
8	Exponential	HR = a(b - exp(-ct))	a = -1.18086 b = 0.9064 c = 0.01064	0.955	-4.7×10^{-6}	0.01061	2.81×10^{-4}
9	Logistic	HR = a/(1 + b exp(-ct))	a = -508.224 b = -4600.22 c = -0.16832	0.888	1.12×10^{-3}	0.01644	6.76×10^{-4}
10	Two-term	HR = a exp(-bt) + c exp(-dt)	a = 0.055275 b = 0.167318 c = 0.055275 d = 0.167318	0.888	1.32×10^{-3}	0.01644	1.35×10^{-3}
11	Diffusion approach	HR = a exp(-bt) + (1 - c) exp(-cdt)	a = -0.53346 b = 0.46365 c = 0.366125 d = 0.999151	0.864	1.37×10^{-3}	0.01227	7.53×10^{-4}

may lead to discontinuities that some authors have attributed to a real discontinuous kinetics in crumb firming (Ovadia and Walker 1996). Crumb firmness data usually fitted to the Avrami (Page model) and modified Avrami (Newton model) equations. These models were derived for crystallization in a restricted solid matrix and have been applied widely for description of staling measurements and crumb firming characterization with limitations in the mathematical analysis (Armero and Collar 1998; Haros *et al.* 2002; Rosell and Santos 2010). However, no attempt has been made so far to modeling the staling kinetic of bread to other mathematical models. The results of the statistical computations undertaken to assess the consistency of 11 staling models for the staling data are presented in Table 6. Regression analyses were done for these empirical models by relating the storage time and dimensionless hardness ratio at each storage time. It can be seen that all models have high values of r and low values of χ^2 , MBE, and RMSE. Based on these results, the models that best fitted the experimental data, considering the statistical tests

applied, were the rational ($r = 0.998$, $MBE = -1.29 \times 10^{-7}$, $RMSE = 0.0023$ and $\chi^2 = 2.65 \times 10^{-5}$) followed by the quadratic model ($r = 0.994$, $MBE = 2 \times 10^{-13}$, $RMSE = 0.0039$ and $\chi^2 = 3.73 \times 10^{-5}$). Thus, the mentioned models are suitable to simulate the staling kinetics of Barbari. It is also observed that consistency of fitting the staling data into these models is very good for all of the experimental conditions. Thus, this model may be assumed to represent the staling behavior of Barbari breads. In particular, the good fit of the Rational model can be related to the presence of its four parameters, which provides a better mathematical approximation on the experimental staling curves.

CONCLUSIONS

Texture analysis was a useful tool to evaluate Barbari flat bread staling, detecting differences among the different kinds and levels of liquid improver components analyzed. The Box-Behnken design was an efficient statistical tool to model

the influence of additives on bread quality, shelf life, sensory and image properties of Barbari bread. These results also suggested that by modifying the proportion of these additives, a large range of variations may be obtained. To simulate the staling behavior of Barbari bread, 11 different models were compared. Based on the statistical tests results, the rational and quadratic models gave the best fits and could be used to accurately predict the hardness of Barbari bread.

REFERENCES

- AACC. 2000. *Approved Methods of the American Association of Cereal Chemists*, American Association of Cereal Chemists, St. Paul, MN.
- ANGIOLONI, A. and COLLAR, C. 2011. Physicochemical and nutritional properties of reduced-caloric density high-fibre breads. *LWT – Food Sci. Technol.* *44*, 747–758.
- ARMERO, E. and COLLAR, C. 1997. Texture properties of formulated wheat doughs relationships with dough and bread technological quality. *Z. Lebensm. Unters. Forsch.* *204*, 136–145.
- ARMERO, E. and COLLAR, C. 1998. Crumb firming kinetics of wheat breads with anti-staling additives. *J. Cereal Sci.* *28*, 165–174.
- AUTIO, K., FLANDER, L., KINNUNEN, A. and HEINONEN, R. 2001. Bread quality relationship with rheological measurements of wheat flour dough. *Cereal Chem.* *78*, 654–657.
- AZIZI, M.H. and RAO, G.V. 2004. Influence of selected surfactant gels and gums on dough rheological characteristics and quality of bread. *J. Food Qual.* *27*, 320–336.
- AZIZI, M.H. and RAO, G.V. 2005a. Effect of storage of surfactant gels on bread making quality of wheat flour. *Food Chem.* *89*, 133–138.
- AZIZI, M.H. and RAO, G.V. 2005b. Effect of surfactant gels on dough rheological characteristics and quality of bread. *Crit. Rev. Food Sci. Nutr.* *44*, 545–552.
- BAIK, M.Y. and CHINACHOTI, P. 2001. Effects of glycerol and moisture gradient on thermomechanical properties of white bread. *J. Agric. Food Chem.* *49*, 4031–4038.
- BARRETT, A.N.N., CARDELLO, A.V., LESHNER, L.L. and TAUB, I.A. 1994. Cellularity, mechanical failure, and textural perception of corn meal extrudates. *J. Texture Studies* *25*, 77–95.
- CABRERA, J.A. and HEEREN, C.W. 1997. Liquid bread improvers. In EP Patent 0,572,051.
- CAMPOS, K.A.D., YOSHINO, C. and HEIN, L.R.D.O. 2009. Fractal behavior throughout stretch zone of 15-5PH steel under elastic-plastic loading conditions. *Mater. Sci. Eng. A* *525*, 37–41.
- CROWLEY, P., SCHOBBER, T., CLARKE, C. and ARENDT, E. 2002. The effect of storage time on textural and crumb grain characteristics of sourdough wheat bread. *Eur. Food Res. Technol.* *214*, 489–496.
- DANIEL, W.W. 1991. *Biostatistics: A Foundation for Analysis in the Health Sciences*, Wiley, New York, NY.
- FARRERA-REBOLLO, R.R., SALGADO-CRUZ, M.P., CHANONA-PÉREZ, J., GUTIÉRREZ-LÓPEZ, G.F., ALAMILLA-BELTRÁN, L. and CALDERÓN-DOMÍNGUEZ, G. 2011. Evaluation of image analysis tools for characterization of sweet bread crumb structure. *Food Bioprocess Technol.* *5*, 474–484.
- GHORBEL, R.E., KAMOUN, A., NEIFAR, M. and CHAABOUNI, S.E. 2010. Optimization of new flour improver mixing formula by response surface methodology. *J. Food Process. Eng.* *33*, 234–256.
- GLIEMMO, M.F., CAMPOS, C.A. and GERSCHENSON, L.N. 2006. Effect of several humectants and potassium sorbate on the growth of *Zygosaccharomyces bailii* in model aqueous systems resembling low sugar products. *J. Food Eng.* *77*, 761–770.
- GODFREY, P. and LIMPET, W. 2002. Soy products as ingredients – farm to the table. *Innov. Food Technol.* *14*, 10–13.
- GOMEZ, M., REAL, S.D., ROSELL, C.M., RONDA, F., BLANCO, C.A. and CABALLERO P.A. 2004. Functionality of different emulsifiers on the performance of breadmaking and wheat bread quality. *Eur. Food Res. Technol.* *219*, 145–150.
- GÓMEZ, M., OLIETE, B., PANDO, V., RONDA, F. and CABALLERO, P. 2008. Effect of fermentation conditions on bread staling kinetics. *Eur. Food Res. Technol.* *226*, 1379–1387.
- GÓMEZ, M., RUIZ-PARÍS, E., OLIETE, B. and PANDO, V. 2010. Modeling of texture evolution of cakes during storage. *J. Texture Studies* *41*, 17–33.
- GRAY, J. and BEMILLER, J. 2003. Bread staling: Molecular basis and control. *Compr. Rev. Food Sci. Food Saf.* *2*, 1–21.
- HALLBERG, L. and CHINACHOTI, P. 1992. Dynamic mechanical analysis for glass transitions in long shelf life bread. *J. Food Sci.* *57*, 1201–1229.
- HAROS, M., ROSELL, C.M. and BENEDITO, C. 2002. Effect of different carbohydrases on fresh bread texture and bread staling. *Eur. Food Res. Technol.* *215*, 425–430.
- HUG-ITEN, S., ESCHER, F. and CONDE-PETIT, B. 2003. Staling of bread: Role of amylose and amylopectin and influence of starch-degrading enzymes. *Cereal Chem.* *80*, 654–661.
- KAMEL, B.S. and PONTE, J.G. 1993. Emulsifiers in baking. In *Advances in Baking Technology*, (B.S. Kamel and C.E. Stauffer, eds.) pp. 113–150, Blackie Academic and Professional, Glasgow, U.K.
- KAMMAN, P.W. 1970. Factors affecting the grain and texture of white bread. *Bakers Dig.* *44*, 34–38.
- MALEKI, M., VETTER, J. and HOOVER, W. 1981. The effect of emulsifiers, sugar, shortening and soya flour on the staling of barbari flat bread. *J. Sci. Food Agric.* *32*, 1209–1212.
- MÄLKKI, Y., PAAKKANEN, J. and EEROLA, K. 1978. Effect of freezing and monoglycerides on staling of bread. *J. Food Process. Preserv.* *2*, 101–110.

- MOHD JUSOH, Y.M., CHIN, N.L., YUSOF, Y.A. and ABDUL RAHMAN, R. 2009. Bread crust thickness measurement using digital imaging and *L a b* colour system. *J. Food Eng.* **94**, 366–371.
- OTSU, N. 1979. Threshold selection method from gray-level histograms. *IEEE Trans. Syst. Man Cybern.* **9**, 62–66.
- OVADIA, D. and WALKER, C. 1996. Re-examination of the bread firming curve. *Starch-Stärke* **48**, 137–144.
- POURFARZAD, A., KHODAPARAST, M.H.H., KARIMI, M., MORTAZAVI, S.A., DAVOODI, M.G., SOURKI, A.H. and RAZAVIZADEGAN JAHROMI, S.H. 2011. Effect of polyols on shelf-life and quality of flat bread fortified with soy flour. *J. Food Process. Eng.* **34**, 1435–1448.
- QUEVEDO, R., DÍAZ, O., CAQUEO, A., RONCEROS, B. and AGUILERA, J.M. 2009. Quantification of enzymatic browning kinetics in pear slices using non-homogenous *L** color information from digital images. *LWT – Food Sci. Technol.* **42**, 1367–1373.
- RAJABZADEH, N. 1991. Iranian flat breads evaluation. Iranian Cereal and Bread Research Institute. Publication 71, 1–50.
- ROSELL, C.M. and SANTOS, E. 2010. Impact of fibers on physical characteristics of fresh and staled bake off bread. *J. Food Eng.* **98**, 273–281.
- RUSSELL, P. 1983. A kinetic study of bread staling by differential scanning calorimetry. The effect of painting loaves with ethanol. *Starch-Stärke* **35**, 277–281.
- SCHIRALDI, A. and FESSAS, D. 2000. Mechanism of staling: An overview. In *Bread Staling*, (P. Chinachoti and Y. Vodovotz, eds.) pp. 1–17, CRC, Boca Raton, FL.
- SUHENDRO, E., WANISKA, R., ROONEY, L. and GOMEZ, M. 1995. Effects of polyols on the processing and qualities of wheat tortillas. *Cereal Chem.* **72**, 122–127.
- TSEN, C. and HOOVER, W. 1973. High-protein bread from wheat flour fortified with full-fat soy flour. *Cereal Chem.* **50**, 7–16.
- ZGHAL, M., SCANLON, M. and SAPIRSTEIN, H. 2002. Cellular structure of bread crumb and its influence on mechanical properties. *J. Cereal Sci.* **36**, 167–176.
- ZHANG, Y.C. 2004. *Physicochemical properties and isoflavone content of bread made with soy*. In PhD Dissertation, The Ohio State University, Columbus, OH.
- ZOBEL, H. and KULP, K. 1996. The staling mechanism. In *Baked Goods Freshness: Technology, Evaluation, and Inhibition of Staling*, (R.E. Hebeda and H.F. Zobel, eds.) pp. 1–64, Marcel Dekker Inc., New York, NY.