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Modelling the browning of bread during baking

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ABSTRACT

In this work, we study the development of browning at bread surface during baking. Computer vision is applied to follow the progress of browning at surface, while the variations of temperature and water activity are obtained by numerical simulation of a mathematical model previously validated. The formation of the bread crust is a complex process where temperature and water content change continuously during baking, making browning a non-isothermal process occurring in a non-ideal system. Minimum requirements for initiation of colour formation are temperature greater than 120 °C and water activity less than 0.6. We apply a non-isothermal kinetics approach to model the browning development at bread surface during baking, where the variation of local temperature and water activity is taken into account. The methodology presented here is suitable for modelling and predicting browning during baking; model parameters can be estimated by using a non-ideal system closer to real processing conditions.

1. Introduction

Bread baking can be defined as the process which transforms a dough basically made of flour, water and leavening agents in a high quality product with unique sensorial features. In particular, French or white bread is the most popular type of bread, and is distinguished for having a crunchy and yellow-gold crust, beyond other features (i.e. a sponge and light crumb with soft texture and intermediate moisture, and a typical flavour). In general, the aspect and colour of food surface is the first quality parameter evaluated by consumers and is critical in the acceptance of the product, since it is associated with flavour and level of satisfaction (Pedreschi, León, Mery, & Moyano, 2006). Therefore, predicting and controlling the development of crust colour are very important issues for the bread making industry.

The formation of the yellow-gold colour often called browning is due to non-enzymatic chemical reactions which produce coloured compounds during bread baking, specifically, the Maillard reaction and caramelization. Maillard browning products (melanoidins) are found where reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together, such as in bread crusts (Fennema, 1996). Besides, the Maillard reaction is associated to a decrease of digestibility and possibly formation of toxic and mutagenic compounds, but also to the formation of antioxidative products (Martins, Jongen, & van Boekel, 2001). Caramelization is a term for describing a complex group of reactions due to direct heating of carbohydrates, in particular sucrose and reducing sugars (Fennema, 1996).

When systems like bread containing reducing sugars and amino groups are heated, caramelization and the Maillard reaction may take place simultaneously (Villota & Hawkes, 2007); both reactions depend on temperature, water activity and pH (Zanoni, Peri, & Bruno, 1995). So, bearing in mind that bread baking is a process where simultaneous heat and mass transfer occurs (Purlis & Salvadori, 2009a), modelling the development of browning during baking becomes a major challenge for food technologists. In this way, some efforts have been made to achieve this aim.

Zanoni et al. (1995) developed a kinetic model for bread crust browning using dehydrated and milled bread crumb as a model system. The proposed model, following first-order kinetics and temperature dependent, was then applied to predict crust browning during bread baking at 200 and 250 °C; results were only acceptable at 250 °C. Ramírez-Jiménez, Guerra-Hernández, and García-Villanova (2000) showed that development of browning can be evaluated effectively from colour measurement during baking and is exponentially correlated with baking time. In addition, crust browning is mainly controlled by temperature (Wählby & Skjöldebrand, 2002). More recently, a brownness model was proposed by assuming an exponential relation between the concentration of melanoidins (produced by Maillard reaction) and colour development at bread surface during baking (Hadiyanto et al., 2007). Also, a simple model depending on the weight loss of bread during baking and the oven temperature is available (Purlis & Salvadori, 2007).

Browning during baking of biscuits has also been studied. Shibukawa, Sugiyama, and Yano (1989) demonstrated that colour

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development depends only on temperature, and a first-order kinetic model, dependent on average temperature and moisture content, was developed to predict lightness variation of cracker surface during baking (Broyart, Trystram, & Duquenoy, 1998). More recently, it was observed that accumulation of 5-hydroxymethyl-2-furfural (HMF) follows first-order kinetics during baking, and is highly dependent on the water activity, which must reach levels lower than 0.4 for allowing a significant formation of HMF (Ameur, Trystram, & Birlouez-Aragon, 2006). Conversely, Mundt and Wedzicha (2007) reported that water activity in the range 0.04–0.15 has not influence on the rate of browning in the baking of biscuits.

So far, it has been well demonstrated that development of browning during bread baking is only dependent on temperature and is caused by a group of complex reactions. Then, colour formation is usually simplified by assuming a general mechanism of browning or else neglecting caramelization (Zanoni et al., 1995). Also, browning kinetics has been modelled by using model systems and/or isothermal experiments. Though considering the actual mechanisms involved in the formation of colour would be the best approach, the chemistry of the browning phenomenon has not been well elucidated yet, being a controversial issue until now (Martins et al., 2001). Nevertheless, it is always useful to search for a mathematical model of browning for technological applications (Keskin, Sumnu, & Sahin, 2004; Therdthai, Zhou, & Adamczak, 2002); such a model would be more accurate if the real process is considered to obtain the browning kinetics. Actually, the formation of the bread crust is a complex process where temperature and water content change continuously during baking (Purlis & Salvadori, 2009a), making browning a non-isothermal process occurring in a non-ideal system. Therefore, we establish the hypothesis that the best predictions for non-isothermal processes are given when non-isothermal methods are used.

As a part of a comprehensive study of the bread baking process (Purlis, 2007), this article deals with the specific objective of developing a methodology for modelling the browning of bread during baking. For this aim, kinetics of colour development was obtained from real experimental conditions by using suitable methods: computer vision was applied to measure browning development, and the thermal history of bread surface was taking into account. In addition, the influence of water activity of bread on colour formation was analyzed in order to contribute to the understanding of the process, mainly from a technological point of view.

2. Materials and methods

2.1. Bread samples

Samples were prepared using a standard recipe for French bread: wheat flour (100%), water (54.1%), salt (1.6%), sugar (1.6%), margarine (1.6%), and dry yeast (1.2%). Dough was made by mixing the ingredients for 10 min in a home multi-function food processor at constant speed. Then, individual samples of 100 g (cylindrical shape, ca. 0.1 m length, and 0.04 m diameter) were formed and placed in a perforated tray. Proving was carried out at ambient temperature covering dough samples with a plastic film in order to prevent dehydration. After 1.5 h proving, samples duplicated their volume. Two samples were prepared for each experiment.

2.2. Baking tests

Dough samples were baked in an electrical static oven (Ariston FM87-FC, Italy) under two different conditions, depending on air velocity: natural convection ($v = 0$ m/s) and forced convection ($v = 0.9$ m/s). Experiments were carried out by using three constant oven temperatures: 180, 200 and 220 °C. Oven air temperature was measured using T-type thermocouples (Omega, USA): the oven allows controlling temperature with ±3.3 °C accuracy. The perforated tray with the samples (2) was placed in the central zone of the oven in order to achieve a homogeneous distribution of heat and mass fluxes. Two tests were performed for each baking condition.

2.3. Crust browning measurement

Detection methods for Maillard reaction and caramelization include colorimetric observation at 420 or 490 nm, chromatographic separation, measurement of carbon dioxide evolution, UV and IR spectrums analysis. However, these techniques are not so useful when colour changes have to be followed during food processing. In this work, we used computer vision (CV) to measure the development of surface browning during bread baking. CV is an automated and cost-effective technique, which has been already applied to evaluate quality features of foods, including bakery products (Brosnan & Sun, 2004). This method is also non-destructive and the measured area in a single determination is higher than that evaluated by a conventional colorimeter. Furthermore, the CV technique does not imply any contact with the sample, which is essential in the case of deformable materials such as bread dough.

The CV system used in this work consisted in a digital camera (Professional Series Network IP Camera Model 550710, Intellinet Active Networking, USA) connected to a PC (AMD Sempron 2200+, 768 MB RAM). The camera lens was located perpendicularly to the surface of bread samples, at 0.4 m distance. Images were acquired under common (non-ideal) light conditions, every 5 min. Since the CV system was placed next to the oven, the image acquisition procedure took about 5 s, thus it is assumed that no significant perturbation was introduced in our experiments.

Once data acquisition was done, image processing was performed. Each image consisted in a *jpg* file of 640 × 480 pixels resolution. Firstly, images were trimmed keeping a major region of bread surfaces, resulting in two rectangular images for each determination, one for each sample (Fig. 1). Then, an algorithm developed in MATLAB 6.5 (The MathWorks, Inc., USA) was used to calculate the colour values; the $L^*a^*b^*$ colour model was chosen to describe browning development. In food research, colour is frequently represented using the $L^*a^*b^*$ colour space, which is an international standard for colour measurements adopted by *Commission Internationale de l'Eclairage* (CIE) in 1976 (Mendoza, Dejmek, & Aguilera, 2007). The three parameters of this model represent the lightness of colour (L^*), which ranges from 0 to 100 (black to white), its position between red and green (a^*, values between −120 and +120) and its position between yellow and blue (b^*, values between −120 and +120) (Yam & Papadakis, 2004). Since digital images are acquired in the RGB colour space (León, Mery, Pedreschi, & León, 2006), the following steps were carried out to obtain the $L^*a^*b^*$ parameters:

1. Image reading (in RGB space).
2. RGB to *XYZ* tristimulus space conversion.

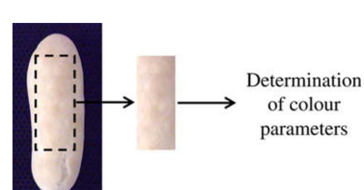

Fig. 1. Schematic procedure for colour determination from the image of bread surface.

3. XYZ to $L^*a^*b^*$ space conversion.
4. Statistics of $L^*a^*b^*$ parameters.

Conversion between colour spaces must be done using a white reference (Gonzalez & Woods, 2002). A perfectly reflecting diffuser under CIE standard $D65$ illumination was taken as white reference, which was defined through its trichromatic values ($x = 0.3127$ and $y = 0.3290$ in the CIE chromaticity diagram). Therefore, steps 2 and 3 were performed as follows:

$$X = 0.4124\, g\left(\frac{R}{255}\right) + 0.3576\, g\left(\frac{G}{255}\right) + 0.1805\, g\left(\frac{B}{255}\right) \tag{1}$$

$$Y = 0.2126\, g\left(\frac{R}{255}\right) + 0.7152\, g\left(\frac{G}{255}\right) + 0.0722\, g\left(\frac{B}{255}\right) \tag{2}$$

$$Z = 0.0193\, g\left(\frac{R}{255}\right) + 0.1192\, g\left(\frac{G}{255}\right) + 0.9505\, g\left(\frac{B}{255}\right) \tag{3}$$

where

$$g(p) = \begin{cases} 100[(p+0.055)/1.055]^{2.4} & \textit{if } p > 0.04045 \\ 100(p/12.92) & \textit{if } p \leq 0.04045 \end{cases} \tag{4}$$

R, G and B are the RGB model components (values from 0 to 255). From tristimulus values (X, Y and Z), $L^*a^*b^*$ parameters were calculated as

$$L^* = 116\, h\left(\frac{Y}{Y_W}\right) - 16 \tag{5}$$

$$a^* = 500\left[h\left(\frac{X}{X_W}\right) - h\left(\frac{Y}{Y_W}\right)\right] \tag{6}$$

$$b^* = 200\left[h\left(\frac{Y}{Y_W}\right) - h\left(\frac{Z}{Z_W}\right)\right] \tag{7}$$

where

$$h(q) = \begin{cases} \sqrt[3]{q} & \textit{if } q > 0.008856 \\ 7.787q + (16/116) & \textit{if } q \leq 0.008856 \end{cases} \tag{8}$$

X_W, Y_W and Z_W are the reference white tristimulus values (Gonzalez & Woods, 2002). Statistics of $L^*a^*b^*$ parameters (step 4) included the mean value and standard deviation calculation. Also, a surface plot and histograms of the colour parameters corresponding to bread images could be easily obtained using computer vision (Purlis & Salvadori, 2007).

Before bread surface colour was measured, a calibration procedure of the CV system was carried out in order to ensure the validity of results. This was done using the calibrating plates of a conventional colorimeter (Minolta CR300, Japan) and adjusting the camera parameters. This calibration (similar to standard colorimeter calibration) was performed previous to each experiment.

2.4. Mathematical model for browning of bread during baking

The development of browning is temperature dependent and occurs when temperature is greater than 110 °C (Mondal & Datta, 2008). Then, only bread surface suffers browning since at surface the temperature increases almost continuously during baking tending to oven temperature, and reaching values greater than 130–140 °C at least (Purlis & Salvadori, 2009a; Zanoni, Peri, & Pierucci, 1993). Note that surface temperature is not constant, but presents a time–temperature or thermal history during the process, i.e. surface heating and thus browning are non-isothermal processes. From this fact, it may not be valid to apply (conventional) isothermal kinetics concepts. In this way, Dolan (2003) reported that highly temperature dependent reactions (such as browning) would be expected to have greater error if time–temperature history is neglected when kinetic parameters are estimated. Therefore, we proposed a non-isothermal kinetics approach to model the colour development at bread surface during baking, where the thermal history is taken into account.

We assumed first-order kinetics for browning, represented by the variation of surface lightness L^*:

$$\frac{dL^*}{dt} = -kL^* \tag{9}$$

The browning rate constant k was related to the bread surface temperature using the following Arrhenius-like expression:

$$k = k_0 \exp\left(-\frac{A}{T(t)}\right) \tag{10}$$

where k_0 and A are fit parameters without physical meaning (van Boekel, 2008). Eq. (10) was chosen since browning was modelled through the change of colour intensity, not directly involving chemical compounds. In this way, it may be not adequate to consider the Arrhenius' law given that the activation energy concept is not associated to our browning kinetics approach. We also included the influence of water activity on browning development in a similar way as Broyart et al. (1998):

$$k_0 = k_1 + \frac{k_2}{a_w(t)} \tag{11}$$

$$A = k_3 + \frac{k_4}{a_w(t)} \tag{12}$$

Note that since both temperature and water activity of bread surface varies with time during baking, an analytical expression for lightness from Eq. (9) cannot be obtained.

Respect to the bread surface temperature, it is well known that is a variable difficult to measure experimentally during the baking process (Zanoni et al., 1995). Actually, placing correctly a thermocouple at the surface of food is not an easy task; moreover, in the case of deformable and low consistency materials changing their volume during processing such as bread dough during baking. Likewise, obtaining the water activity (or moisture content) variation of bread crust during baking is also complicated. Such measurement requires the setting up of a (destructive) method for accurate sampling while bread is still hot and deformable, and the minimization of water losses by evaporation from cut surfaces (Wagner, Lucas, Le Ray, & Trystram, 2007). To solve these problems, we used a previously validated mathematical model for bread baking to obtain temperature and water activity values at bread surface by means of numerical simulation. For a detailed description about baking simulation, the reader is referred to Purlis and Salvadori (2009b).

3. Results and discussion

A first assessment of the development of browning at bread surface during baking can be done by visual inspection of the images

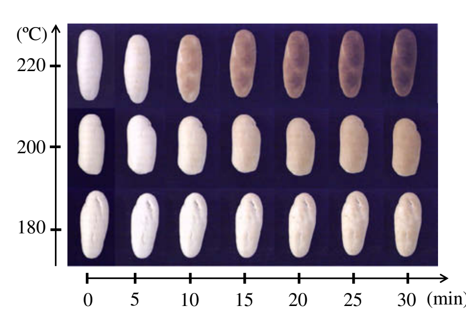

Fig. 2. Image gallery of bread samples baked at 220 °C under natural convection. x-Axis represents baking time and y-axis the oven temperature.

acquired by the CV system (Fig. 2). It can be seen that the colour intensity of samples increased with baking time, as is expected. However, browning was only evident since 10 min baking for 200 and 220 °C oven temperature, and since 15 min for 180 °C. Besides the notable influence of oven temperature on colour development, it was observed a difference in the achieved darkness of samples when 220 °C was used for baking, where breads seemed to be burnt at the end of baking. Note that though images from natural convection baking mode are only depicted, a similar trend was found for forced convection settings.

After image acquisition and processing were performed, $L^*a^*b^*$ parameters were calculated by Eqs. (1)–(8) for each pixel of each sample image. In summary, for each sampling time, the mean values of the colour parameters were obtained from four different images involving almost 10^5 pixels every time (this value depends on image resolution settings when acquisition is made). This demonstrates the advantage of using a CV system over other colorimetric techniques, since it allows handling a large amount of data for each determination, besides it is a rapid and non-destructive method. Despite the fact that all three parameters of the CIE model were evaluated, the subsequent analysis of the development of browning was based on L^* variation of samples during baking (Broyart et al., 1998; Ramírez-Jiménez et al., 2000; Shibukawa et al., 1989). Lightness is a good descriptor of the browning progress since it represents the intensity of images, and is decoupled from colour changes denoted by a^* and b^* values (Gonzalez & Woods, 2002).

Fig. 3 shows the variation of lightness of bread crust for all six baking conditions. As previously described through images, the samples became darker with baking time and with increasing oven temperature. In addition, surface temperature data was obtained by numerical simulation of the baking process using the same operative conditions as in experimental tests (Fig. 4). Relating these two figures, it is clearly shown that browning development depends on temperature.

Two stages could be distinguished in the variation of lightness during baking. During the first minutes, the surface of bread showed an enlightenment respect to initial time (raw dough) when baking at 180 and 200 °C under natural convection and 180 °C under forced convection (Fig. 5). This observation seems to be absurd, since this phenomenon is against browning development. However, other authors also found this result: Shibukawa et al. (1989) attributed this behaviour to surface drying, while Broyart et al. (1998) proposed the contribution of initial volume change as well. Probably, this meaningless phenomenon is related to physical changes occurring at product surface and the method used for measurement of colour formation. At the end of proving, the surface of bread is wrinkled, irregular, but after a few minutes (2 or 3 min) of baking, it turns considerably smooth due to volume increase. This change in surface texture may be the reason of the observed initial enlightenment, since it is well known that a smooth regular surface can reflect more amount of light than a wrinkled irregular one, which is then captured by the computer vision technique. So, this first stage is certainly a lag phase where the food system conditions are not sufficient for allowing browning reactions to start.

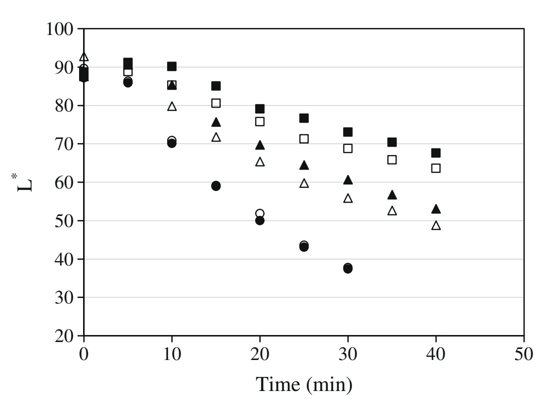

Fig. 3. Variation of lightness (L^*) at bread surface as a function of baking time. Squares represent 180 °C, triangles 200 °C and circles 220 °C. Filled symbols show natural convection data and unfilled symbols forced convection data.

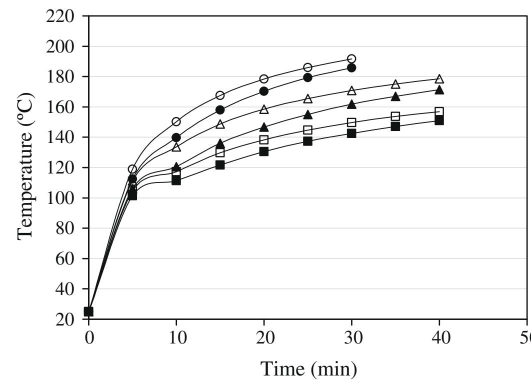

Fig. 4. Surface temperature profiles (obtained by simulation) at bread surface during baking. Squares represent 180 °C, triangles 200 °C and circles 220 °C. Filled symbols show natural convection data and unfilled symbols forced convection data.

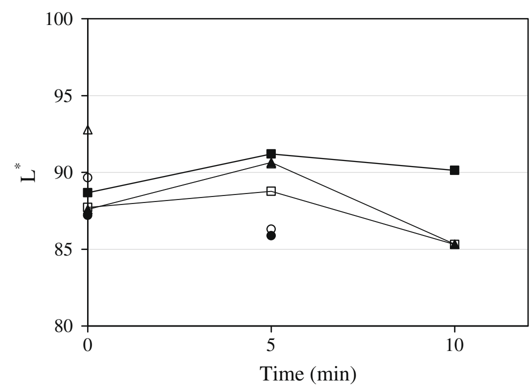

Fig. 5. Lightness of bread surface during the first stage of browning. Solid lines indicate the conditions where enlightenment is observed. Squares represent 180 °C, triangles 200 °C and circles 220 °C. Filled symbols show natural convection data and unfilled symbols forced convection data.

In fact, it has been shown that some requirements must be accomplished to initiate colour formation. In biscuit baking, Shibukawa et al. (1989) reported a decrease in lightness when surface temperature reached 120 °C, while Broyart et al. (1998) found a temperature range of 105–115 °C for the on-set of browning, and Wählby and Skjöldebrand (2002) stated that browning of buns crust begins when the temperature is greater than 110 °C. In this work, we observed that browning is initiated when surface temperature exceeds 120 °C (Figs. 3 and 4). Furthermore, the beginning of browning is highly dependent on the water activity of product. Ameur et al. (2006) reported that the formation of HMF in biscuits starts from an average water activity of 0.40, and that low water content strongly favours HMF formation since less energy activation is involved. Similar critical values for water activity were found in the present study, where results were obtained by numerical simulation (Fig. 6).

Then, the second stage is characterized by the darkening of bread surface. In the same way as baking, the formation of colour is a simultaneous heat and mass transfer process: the increase of

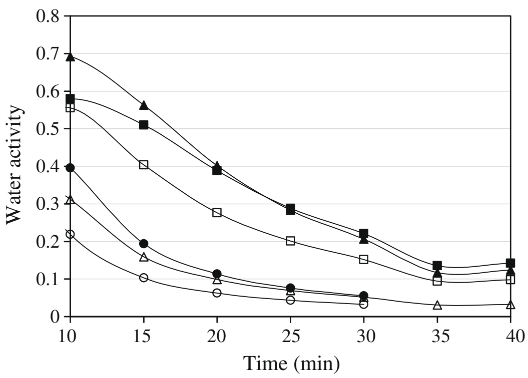

Fig. 6. Water activity at bread surface during the darkening phase. Squares represent 180 °C, triangles 200 °C and circles 220 °C. Filled symbols show natural convection data and unfilled symbols forced convection data.

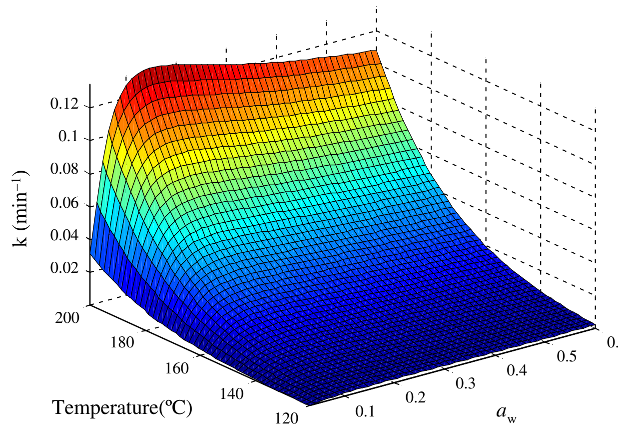

Fig. 7. Variation of the browning rate constant k with temperature and water activity (Eq. (13)).

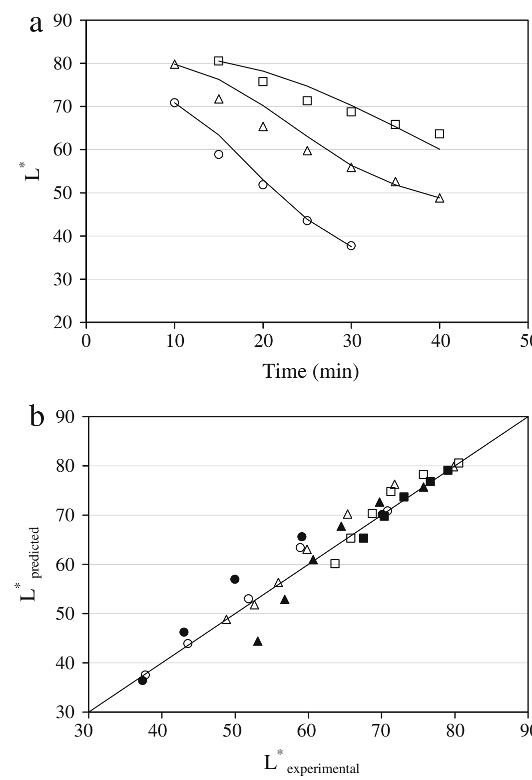

Fig. 8. (a) Lightness of bread surface as a function of time during baking under forced convection; solid lines represent regression results obtained from Eqs. (9)–(12). (b) Comparison between experimental and predicted lightness; solid line accounts for the perfect prediction. Squares represent 180 °C, triangles 200 °C and circles 220 °C. Filled symbols show natural convection data and unfilled symbols forced convection data.

temperature at surface generates the evaporation of unbound (free) water decreasing the moisture content and subsequently, the water activity of the crust, which accelerates the Maillard reaction giving more melanoidins during baking (Hadiyanto et al., 2007). Moreover, when temperature is very high and low water activity is achieved, caramelization takes place producing more coloured compounds in addition to Maillard reaction products. This drastic condition at surface is responsible of the burnt appearance and low lightness values of samples baked at 220 °C (Figs. 2 and 3).

Finally, we obtained the kinetic model for browning of bread during baking. Based on previous discussion, only data from the darkening phase was considered, i.e. lightness values corresponding to surface temperature greater than 120 °C. The kinetics parameters (k_1, k_2, k_3, and k_4) from Eqs. (11) and (12) were estimated by non-linear regression using a Levenberg-Marquardt algorithm (function *lsqcurvefit* from MATLAB). The first-order differential equation describing lightness variation (Eq. (9)) was evaluated numerically using a medium order Runge–Kutta routine (function *ode45* from MATLAB). So, the final expression for the browning rate constant (k, min^{-1}) as a function of water activity and temperature (K) at bread surface is the following:

$$k = \left(7.923310^6 + \frac{2.739710^6}{a_w}\right) \exp\left(-\frac{\left(8.701510^3 + \frac{49.4738}{a_w}\right)}{T}\right) \tag{13}$$

The influence of both water activity and temperature on browning rate is shown in Fig. 7. As was explained, browning is highly dependent on temperature, but also on water availability at bread surface. Note that the model well reproduces the experimental observation that low water content strongly favours the formation of HMF and more colour compounds via caramelization; this can be seen in the a_w range of 0.1–0.2 in Fig. 7 (for constant temperature, Eq. (13) always shows a maximum in this a_w interval).

The goodness of the model prediction was assessed by the mean absolute relative error defined as

$$e_{abs}(\%) = \frac{100}{n} \sum_{i=1}^{n} \left(\frac{|L^*_{experimental} - L^*_{predicted}|}{L^*_{experimental}}\right)_i \tag{14}$$

where n is the number of output values taken into account. Fig. 8a shows the regression results for the forced convection baking condition (similar results were found for natural convection), while Fig. 8b depicts the overall performance of the obtained model. As can be seen, the model well adjusted the experimental data, indicating that the assumption of first-order kinetics for lightness decrease is correct. Moreover, the mean error calculated by Eq. (14) was equal to 3.6095% ($n = 34$).

4. Conclusions

The development of browning in bread during baking is a dynamic process which depends on local temperature and water activity. Minimum requirements for initiation of colour formation are temperature greater than 120 °C and water activity less than 0.6. Furthermore, there would be some drastic conditions, i.e. high temperature and low water activity, where high browning rates are achieved, particularly when caramelization occurs.

The methodology presented in this work, i.e. computer vision, numerical simulation and non-isothermal kinetics, is suitable for modelling and predicting the browning of bread during baking. Though numerical results are difficult to extrapolate, we hope the approach applied here will be useful for other experiments or operative conditions of bread baking, as well as for other bakery products. Besides the non-isothermal approach is conceptually the most adequate since a non-isothermal process is being studied, it should be noted the advantage of estimating parameter from a non-ideal system closer to industrial real processing conditions.

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