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Modelling of Browning Kinetics of Bread Crust During Baking

B. Zanoni, C. Peri and D. Bruno

DISTAM, Sezione Tecnologie Alimentari, Università di Milano, Via Celoria, 2 I-20133 Milano (Italy)

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A mathematical model was set up to predict browning kinetics of bread crust during baking. A bread dough was placed into a cylindrical steel mould and baked in a pilot forced-convection oven at 200 and 250°C. The sample surface temperature was measured using both a type J thermocouple and an infrared thermometer. Surface browning (ΔE) of bread crust during baking was measured by a tristimulus colorimeter. The kinetic model for bread crust browning was obtained by instant heating of dried crumb on contact with a refractory plate at 140, 150, 165, 185, 210, 235 and 250°C. At all temperatures ΔE tended asymptotically to $\Delta E_\infty = 52$, which corresponded to the burnt sample. The colour difference varies as a function of first-order kinetics. The rate constant k depends on temperature according to the Arrhenius equation ($k_o = 42{,}000\ s^{-1}$; $E_a = 64{,}151$ J/mol). Kinetics was validated under dynamic temperature conditions: the experimental results were compared with those obtained from a mathematical model for heat and mass transfer during baking connected to the kinetic model for browning.

Introduction

Surface colour is an important characteristic of baked products because it, together with texture and aroma, contributes to consumer preference. Surface colour depends both on the physico-chemical characteristics of the raw dough (i.e. water content, pH, reducing sugars and amino acid content) and on the operating conditions applied during baking (i.e. temperature, air speed, relative humidity, modes of heat transfer). From a technological point of view, obtaining a particular colour at the product's surface is one of the objectives of baking. Hence, surface colour may be considered a critical index of baking.

In recent years, surface colour control has involved the setting up of instruments for off-line and on-line colour measurement (1). Also, new baking plants and methods (i.e. IR baking) and new product formulations have been developed to obtain better colour control.

Kinetic studies on the prediction of surface colour development have not been very successful.

Chemical reactions, which cause browning of baked products during baking, include Maillard reactions and caramelization.

Studies carried out using model solutions of reducing sugars and amino acids, mainly glucose-glycine and glucose-lysine, have shown that the formation of brown products in Maillard reactions follows zero-order kinetics (2–6).

Caramelization depends on direct degradation of sugars due to heat. Pilar Buera *et al.* (4–6) showed that model solutions of fructose, xylose and maltose follow zero-order kinetics, whereas model solutions of glucose, lactose and saccharose follow a fractional order kinetic model ($\approx$0.5).

Both Maillard reactions and caramelization depend on type of reagent, temperature, water activity and pH. It is evident that the kinetic study is more complex when, as for baked products, the complex sugar and amino acid mixture is heated to high temperatures and, consequently, Maillard reactions and caramelization occur simultaneously. This phenomenon becomes even more complex during baking, when the surface of baked products (i.e. the crust) is subject to variations in temperature and water activity. In such cases, kinetics is usually simplified in two ways as follows: (a) overall browning kinetics is studied, while neglecting individual reaction mechanisms; (b) caramelization is considered negligible.

Hermann and Nour (7) studied surface browning kinetics for doughs made from flour and water during baking at 150, 170 and 190°C. Browning was measured by spectrophotometry at 420 nm using a water solution of coloured compounds, obtained by mixing with water and subsequent filtration of the browned doughs. Experimental tests showed that browning kinetics is characterized by a lag phase (detected at 150°C), followed by an exponential phase (detected at the three temperatures) and an asymptotic phase (detected at 190°C). According to Hermann and Nour (7), who neglected caramelization, the above-mentioned behaviour is due to Maillard reactions, described as consecutive reactions:

$$A + K \ldots \xrightarrow{k_1} Z \xrightarrow{k_2} P \xrightarrow{k_3} M \qquad \text{Eqn [1]}$$

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The reaction between amino acids (A) and reducing sugars (K) yields intermediate products (Z). These result in water-soluble coloured products (P), which change into insoluble coloured compounds, namely melanoidins (M). The browning reaction, after the lag phase, can be described by first-order kinetics for the formation of compounds P (i.e. exponential phase) when $k_2 > k_3$, and then by the combination of kinetics for the formation of compounds P and M when $k_2 \cong k_3$ (i.e. asymptotic phase).

Shibukawa *et al.* (8) investigated the effect of heating by convection and radiation in an oven, at 180°C to 240°C, on the surface colour of biscuits. This colour was compared with browning of a model solution of monosodium glutamate and glucose, which followed first-order kinetics.

In previous works, Zanoni *et al.* (9, 10) set up a mathematical model for baking, which allowed the prediction of heat and mass transfer inside the product and at the product's surface during baking. This model was subsequently correlated to starch gelatinization kinetics as an index of the degree of baking of the crumb. The model was validated for baking of chemically leavened bread (11).

The aim of this work is to set up and validate a kinetic model for browning of bread crust, correlated to the above-mentioned baking model, which can be used as an index of the degree of baking of the crust.

Materials and Methods

Bread sample preparation and baking

210 g flour (92.9 g/kg moisture, 130 g/kg proteins on dry basis, 6.0 g/kg ash on dry basis), 126 g water, 8.4 g leavening powder (A. Bertolini Srl, Collegno, Torino, Italy) and 4.2 g salt were mixed in a Hobart N50G kneading machine at room temperature for 5 min.

The dough was cut and then placed into a cylindrical steel mould (5.44 cm in height, 7.36 cm in diameter). The sample surface was smoothed to facilitate subsequent measurements for surface colour. Finally, thermocouples were placed into the dough to measure surface temperature. The time required was 15 min at room temperature.

Baking was carried out in a pilot forced-convection electric oven (Carlo Erba, Milano, Italy) at 200 and 250°C for increasing time intervals up to 1 h.

Measurement of temperature

The air temperature, the temperature of oven walls and the temperature at the sample's surface were measured. The oven temperature was measured using a type J thermocouple (0.5 mm in diameter). Oven wall temperatures were also measured using the above-mentioned self-adhesive thermocouples type J (Tersid, Milan, Italy). The sample surface temperature was measured using (a) a type J thermocouple (0.5 mm) and (b) an infrared thermometer.

(a) A type J thermocouple was used, which was placed on the central axis of the sample at the upper surface under a thin dough layer.

(b) The surface temperature was measured using a Thermopoint TPT200L TSF/CF infrared thermometer (AGEMA Infrared System Srl, Milano, Italy). This instrument was equipped with a cooling water jacket at 2 L/min flow rate and a temperature of 10 to 27°C. The thermometer was suspended outside the oven using a wall mechanic arm. A special lid with a hole (35 mm in diameter) was placed on the oven. The thermometer was placed on the lid hole at 33 cm distance from the sample surface, which corresponded to 24 mm spot diameter. Both the thermocouples and the infrared thermometer were connected to a data acquisition and recording system (Datascan 7720, Datagest Srl, Milano, Italy) interfaced by RS232 to a PC. All measurements of temperature were carried out in quintuplicate.

Measurement of surface browning

Surface browning of bread crust samples was measured by the Hunter colorimetric system using a Minolta Chroma Meter CR-210 tristimulus colorimeter (Barletta Srl, Milano, Italy) and expressed as colour difference ΔE between the raw dough and the samples subjected to heating according to the following equation (12):

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \qquad \text{Eqn [2]}$$

where: ΔL = brightness difference; Δa = redness difference; Δb = yellowness difference.

The tests were carried out under the following time and temperature conditions: at 200°C for 5, 10, 15, 20, 25, 30, 35, 40, 50, 60 min and at 250°C for 2, 4, 7, 10, 12, 14, 18, 21, 30, 35, 50, 45, 50, 60 min. At each time–temperature combination the bread sample was removed from the oven and surface colour was immediately measured upon contact with the colorimeter surface. The sample was then discarded. All tests were carried out in duplicate.

The same method, applied to commercial breads, showed that crust colour of commercial breads varies from a minimum $\Delta E = 4$ to a maximum $\Delta E = 31$ according to the type of bread. Most samples had a ΔE value between 20 and 27.

Model for heat and mass transfer during baking

This model is based on phenomenological hypothesis, equations and boundary conditions reported in previous papers (9, 10). The equations for the overall heat exchange coefficient and the equations for the apparent density and the thermal conductivity of the sample

Table 1 Constant properties for solving the mathematical model

Sample weight	110 g
Sample radius	36.8 mm
Sample initial height (Ho)	32 mm
Sample initial temperature	24 °C
Sample initial moisture	40.94%
Sample emissivity	0.95
Thickness of lateral mould wall	0.35 mm
Thickness of lower mould wall	0.4 mm
Thermal conductivity of the mould	45 W/(m.K)
Relative humidity	70%
Convective heat transfer coefficient	20 W/(m^{2}K)
Convective mass transfer coefficient	4 10^{-2} m^2/s
Baking time	Variable up to max 60 min

Table 2 Variable properties for solving the mathematical model

	Air	Upper and lateral walls	Lower wall
Oven temperature	200°C 250°C	190°C 234°C	208°C 262°C
Sample height variation kinetics with baking time	200°C	for $0 \leq t \leq 600$ s	H_t/H_o=8.69 $10^{-4}\,t$+1
		for $t > 600$ s	H_t/H_o=1.78
	250°C	for $0 \leq t \leq 600$ s	H_t/H_o=0.125 $10^{-2}\,t$+1
		for $t > 600$ s	H_t/H_o=1.78

were revised. The model was validated. It allowed us to predict the crumb temperature of chemically leavened bread samples adequately (11).

A numerical computer model in Fortran programming language was set up and a PC was used to solve the mathematical model.

The symmetric heating of the sample, which has been verified in a previous work (9), facilitates solving of the mathematical model in the same way for any rectangular cross-section of the finite cylinder.

Each cross-section is divided into a grid system whose nodes represent the points of calculated temperature and moisture of the product. Nodes are marked with **I** and **J** to show the sequence of vertical and radial volume elements, respectively. The above-mentioned equations were solved by the numerical explicit solution by finite differences. These equations represent the core of the numerical computer model that permits the determination of sample moisture and temperature of each node at given time intervals.

Boundary conditions are:

$$\begin{array}{lll}
\text{at } t = 0 & T = T_o & \text{for } 0 \leq r \leq R \text{ and } 0 \leq x \leq H \\
& W = W_o & \text{for } 0 \leq r \leq R \text{ and } 0 \leq x \leq H \\
\text{at } t > 0 & T = T_{ss} & \text{for } r \leq R \text{ and } 0 \leq x \leq H \\
& T = T_{ss} & \text{for } x = 0 \text{ and } 0 \leq r \leq R \\
& T = T_{ss} & \text{for } x = H \text{ and } 0 \leq r \leq R \\
& dT/dr = 0 & \text{for } r = 0 \\
& dW/dr = 0 & \text{for } r = 0
\end{array}$$

where H is the height, R is the radius of the sample, T is the temperature, T_0 is the initial temperature, T_{ss} is the surface treatment, W is the absolute humidity, W_0 is the initial absolute humidity and W_{ss} is the surface absolute humidity.

Table 1 and **Table 2** show data and equations for solving of the model.

Kinetic model for bread crust browning

This model is based on the kinetic determined by Gianotti (13) according to the method reported below.

The study of browning kinetics was carried out using ground, dried bread crumb. The dough, prepared using the same ingredients described above, was baked at 100°C for 1 h in order to obtain bread crumb and avoid crust formation.

After cooling at room temperature, the crumb was ground using a mill (Waring Commercial Blendor) at speed 1 for 15 s. Subsequently, the ground crumb was placed in 1 cm thick layers into glass dishes (9 cm in diameter, 1 cm in height) and compressed gently to obtain small, flat, firm discs. The samples in the dishes were dried in an oven at 102°C until reaching constant weight (about 4 h).

In order to measure browning kinetics of the crumb, a method for instant heating of samples on contact with a refractory plate was set up. Browning tests were carried out on the dried crumb under the following temperature conditions of the refractory: 140, 150, 165, 185, 210, 235 and 250°C. Sample surface browning was measured using the same method described in the section 'Measurement of surface browning'. The temperature of the refractory was controlled by a self-adhesive thermocouple type J (0.5 mm).

At all temperatures ΔE tended asymptotically to $\Delta E_\infty = 52$, which corresponded to the burnt sample. The colour difference ΔE was well correlated ($r = 0.99$) to the heating time according to the following relationship:

$$\Delta E\infty - \Delta E = \exp(-kt) \qquad \text{Eqn [3]}$$

where: ΔE_∞ = asymptotic ΔE value; ΔE = ΔE of the sample at time t; k = reaction rate constant (s^{-1}); t = time (s)

It was found that the reaction rate constant depends on temperature according to the Arrhenius equation ($r = 0.99$):

$$k = k_o \exp\left(\frac{E_a}{RT}\right) \qquad \text{Eqn [4]}$$

with k_o = 42,000 s^{-1} and E_a = 64,151 J/mol.

This model was applied to predict crust browning during baking. This was obtained from the sum of the various ΔE values with respect to each finite time increase Δt. k was calculated at the temperature of a specific point of the product surface by the Arrhenius equation.

Browning resulting from each time interval was calculated and added to that of previous time intervals as follows:

$$\Delta E_{(I,J)t} = \Delta E_{\infty} - \left(\left(\Delta E_{\infty} - \Delta E_{(I,J)t-\Delta t} \right) \exp\left(-k_{T(I,J)} \Delta t\right) \right) \qquad \text{Eqn [5]}$$

This model can be applied both to experimental temperature profiles and to temperature profiles calculated according to the model for heat and mass transfer described above. In the former, Δt is equal to the time interval between two temperature measurements (in our case 10 s); in the latter, Δt is equal to the time interval applied to solve equations of our model (in our case 0.1 s).

Results and Discussion

Prediction of surface temperature

In order to validate browning kinetics, it was necessary that the model for heat and mass transfer should predict the trend of the surface temperature of bread during baking adequately. To this end, an accurate method was required to measure the surface temperature of the sample.

Figure 1 shows a comparison between surface temperature profiles determined with the infrared thermometer and with the type J thermocouple during baking at 250°C. It can be observed that the range of values ($\bar{x} \pm S_x$) around the average profile is much more limited for the data obtained using the infrared thermometer than for those obtained using the type J thermocouple. Therefore, it can be concluded that the infrared thermometer provides more reproducible data than the type J thermocouple. The higher experimental error of thermocouple data depends on the low accuracy in positioning the thermocouple just at the product's surface.

From **Fig. 1** it can also be seen that the average surface temperature measured with the type J thermocouple is lower than that measured with the infrared thermometer. This depends on the fact that the thermocouple should be positioned under a thin dough layer, which does not allow the real surface temperature to be measured. On the other hand, if the thermocouple is placed at the sample's surface, one may measure the oven air temperature instead of the sample surface temperature. Similar results were also obtained for the experiments carried out at 200°C.

The experimental temperature profiles were used to validate the mathematical model for heat and mass transfer. **Figure 2** shows a comparison between the experimental surface temperature profiles measured with the infrared thermometer and those calculated by the mathematical model during baking at 200°C. It can be observed that the calculated temperature profile closely follows the trend of the experimental profile. This demonstrates that the model stimulates the evolution of the surface temperature of the product adequately. In fact, the gap between calculated and experimental values is within the experimental error of temperature measurement.

The trend of the predicted temperature profile tends to be stepwise, not continuous. This behaviour depends on the phenomenological hypothesis of the evaporation front at 100°C, which is the basis of our model. Whenever a layer underlying the product's surface reaches 100°C, a step is formed, which holds as long as the layer remains at 100°C. This difference between the calculated and the experimental trend becomes less evident with increasing the dimension of the matrix I, J,

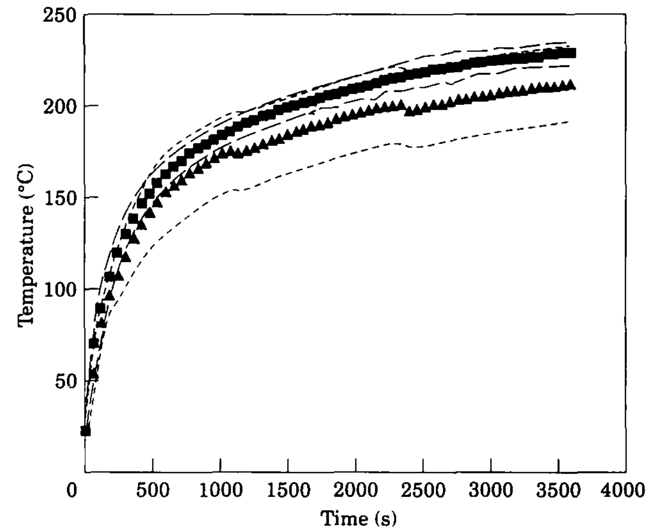

Fig. 1 Comparison between surface temperature profiles measured by IR thermometer and those measured by thermocouple for baking tests at 250°C (■ = average temperature profile (IR thermometer): (|— — —|) 95% confidence level; ▲ = average temperature profile (thermocouple): (|- - - - -|) 95% confidence level)

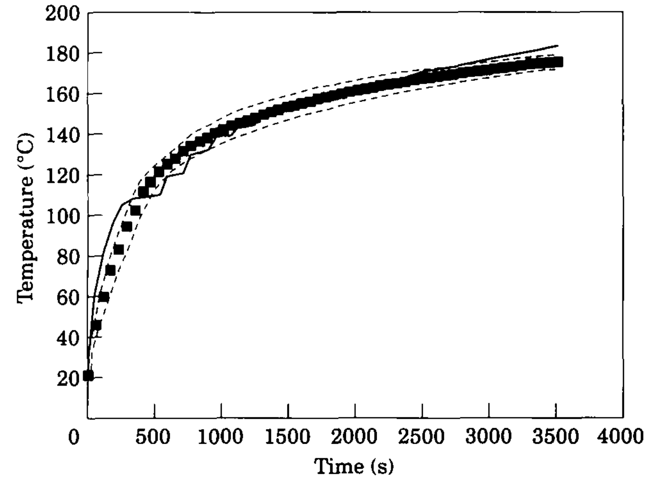

Fig. 2 Comparison between experimental and calculated surface temperature profiles for tests at 200°C (■ = average experimental temperature profile; |- - -| = 95% confidence level of the experimental temperature; |—| = calculated temperature profile)

into which the product is subdivided to solve the model.

Validation of the kinetic model for surface browning

Figures 3 and **4** show the evolution of calculated and experimental values for crust colour at an oven temperature of 200 and 250°C, respectively. The mathematical model adequately simulates the real phenomenon at an oven temperature of 250°C, while calculated and experimental tends clearly diverge at 200°C. In this case, the experimental values trend to an asymptote between 25 and 30 ΔE, while the asymptote of the calculated trend is $\Delta E = 32$ at both temperatures. Consequently, the assumption that the same ΔE can be used in a wide range of temperatures, which was found acceptable in our isothermal browning experiments, cannot be applied to practical baking conditions. Variations in the water content of the crust during baking may account for the differences with the isothermal experiments, which were carried out on dry samples. However, if one considers that practical bread-baking allows a maximum ΔE of about 30 to be reached, the mathematical model set up in this work may prove to have an acceptable predictive ability. Up to a ΔE value of about 30, calculated and experimental ΔE values are in good agreement at both temperatures.

Conclusions

The following conclusions can be drawn from this work:

The mathematical model for heat and mass transfer in the bread crust during baking is adequate. It appears to be more reliable and flexible than other models reported in the literature.

The crust browning model, though oversimplified, proved valid in predicting the experimental trend of browning in the range of crust colour which includes traditional values for commercial breads.

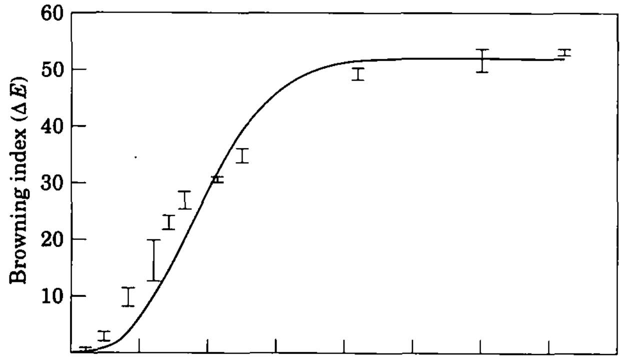

Fig. 3 Validation of the browning profile for tests at 250°C (|—| = calculated profile; I = experimental data for browning)

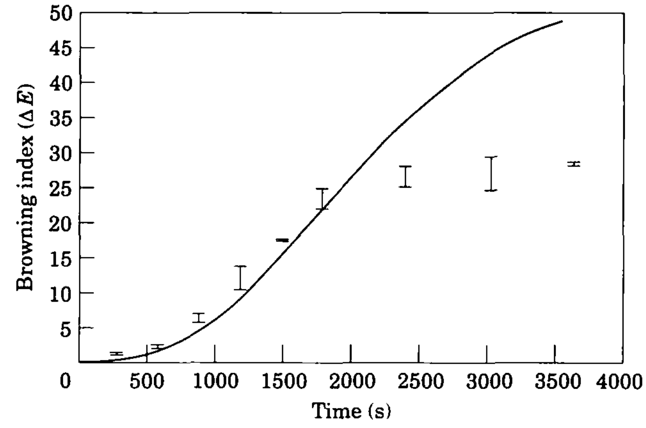

Fig. 4 Validation of the browning profile for tests at 200°C (|—| = calculated profile; I = experimental data for browning)

However, the crust browning model needs further refinement and validation. Obviously, this paper has a merely methodological purpose. Kinetic constants of the browning reaction during baking are different for different products. They depend on composition, especially on the concentration of reducing sugars and amino groups.

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