Lebensm.-Wiss. u.-Technol., 28, 314–318 (1995)

Modelling of Starch Gelatinization Kinetics of Bread Crumb during Baking

B. Zanoni, C. Peri and D. Bruno

Distam, Sezione Tecnologie Alimentari, Universita' di Milano, Via Celoria, 2, I-20133 Milano (Italy)

(Received June 16, 1994; accepted December 15, 1994)

A mathematical model was set up to predict the extent of gelatinization of starch in bread crumb during baking. A bread dough was placed into a cylindrical steel mould and baked in a pilot forced-convection electric oven at 250 °C. A type J thermocouple was placed into the bread crumb (i.e. at a depth of 22 mm in axial position) in order to measure the temperature. Samples were extracted at different final baking temperatures (60, 65, 70, 75, 77, 80, 85, 90, 95, 98°C) and the determination of starch gelatinization kinetics was carried out on differential scanning calorimetric traces. It was shown that the extent of starch gelatinization follows first-order kinetics, where the rate constant varies with temperature according to the Arrhenius equation ($K_o = 2.8\ 10^{18}\ s^{-1}$; $E_a = 138$ *kJ/mol). Kinetics were 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 gelatinization.*

Introduction

Baking is based on simultaneous heat and mass transfer, which causes a progressive increase of temperature and dehydration of the product. Such phenomena determine the kinetics of a series of complex chemical reactions (i.e. volume increase, starch gelatinization, gluten denaturation and surface browning) responsible for the formation of bread crust and crumb having special sensory characteristics for texture, crispness, surface colour and flavour.

In order to control efficiently and optimize baking, one should clearly identify critical phenomena which determine the quality of the final product, and their kinetics under various baking conditions.

For baked products with a soft, wet crumb, such as bread, starch gelatinization, together with protein coagulation, formation of a brown crust and formation of flavour compounds, are critical factors in baking (1). In fact, starch gelatinization is one of the factors that determine the baking time. Complete starch gelatinization in the crumb should be considered the first quality index of soft baked products. If starch gelatinization does not occur, sensory acceptability of the product, in terms of both appearance and texture, will never be ensured. Consequently, the extent of gelatinization may be taken as a 'minimum baking index' (i.e. a control parameter of the baking process). Complete starch gelatinization must first be reached in the product, and a flavoured, coloured crust then forms.

Starch gelatinization has been studied by many workers, who advanced hypotheses about its molecular mechanism and studied the influence of some components of baked products, such as water, lipids, sugar, and salts, on the phenomenon (2–5).

The molecular mechanism is uncertain. According to a more recent hypothesis (4), starch is a dispersion of amylopectin crystals and amylose within a non-crystalline (amorphous) matrix. Gelatinization would be characterized by two closely correlated phenomena: glass transition of the amorphous component and melting of the crystalline component.

According to most authors (6), starch gelatinization in water/starch systems follows this kinetic model:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \qquad \text{Eqn [1]}$$

where A represents ungelatinized starch, R swollen granules, and S solubilized starch. Both phases are irreversible and follow first-order kinetics of the form:

$$\frac{dC_A}{dt} = -k_1 C_A \qquad \text{Eqn [2]}$$

$$\frac{dC_S}{dt} = -k_2 C_R \qquad \text{Eqn [3]}$$

where k_1 and k_2 are the reaction rate constants, which depend on temperature, according to the Arrhenius equation.

If the initial concentration of ungelatinized starch is C_{A_0}, the kinetic model is:

$$\alpha = \frac{C_S}{C_{A_0}} = 1 + \frac{k_2}{k_1 - k_2}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t) \qquad \text{Eqn [4]}$$

where α is the gelatinized starch fraction. If the rate of swelling of starch granules is much faster than their

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dispersion rate, the dispersion rate controls the reaction.

Some authors applied this kinetic theory to the molecular phenomenology of starch gelatinization (4). According to Lund and Wirakartakusumah (7), who have studied rice starch gelatinization kinetics by differential scanning calorimetry (DSC), gelatinization follows first-order kinetics only beyond a certain extent of gelatinization. During the initial phase of heating, to slightly above 65 °C, gelatinization would only affect the amorphous regions and would not follow first-order kinetics. During the subsequent phase of the process, the crystalline regions, destabilized by the amorphous component, 'melt' according to first-order kinetics.

Zanoni *et al.* (8) set up a model of starch gelatinization kinetics for bread. Calorimetric traces, after smoothing and standardization, were deconvoluted into one or two Gaussian curves, depending on the treatment temperature and time. This suggested that the system is a mixture of two components, the second of which was found to have a lower gelatinization rate. The kinetic parameterization was only applied to the second Gaussian curve. It was shown that the trend of the second peak fits well with first-order kinetics, where the rate constant varies with temperature according to the Arrhenius equation ($K_o = 2.8\ 10^{18} s^{-1}; E_a = 138$ kJ/mol).

A large number of kinetic models for gelatinization are found in the literature. Conversely, few studies are available on the use of these kinetic models to control and predict baking of products. A kinetic model is required, which can be used at varying temperatures (i.e. a dynamic model), and which allows the prediction of the temperature profile at various points of the product during baking.

The aim of this work is to validate the gelatinization model, set up in a previous study (8), and to correlate it with a model used to predict heat and mass transfer during bread baking, which is a modified form of the model by Zanoni *et al.* (9, 10).

Materials and Methods

Determination of the extent of gelatinization during baking

210 g flour (92.9 g/kg moisture, 130.0 g/kg proteins on dry basis, 6 g/kg ash on dry basis, pH 5.7–6.1), 16 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 for 5 min. Water was added as required to form a dough having a final consistency of 500 Brabender Units.

The dough was placed into a cylindrical steel mould (5.44 cm in height, 7.36 cm in diameter) and kept at room temperature for 15 min before being baked. Baking was carried out in a pilot forced-convection electric oven (Carlo Erba, Milano, Italy). The air temperature was kept at 250 ± 1 °C. A type J thermocouple (0.5 mm in diameter), connected to a data acquisition and recording system (Datascan 7220 — Measurement Systems Limited, Newbury, U.K.) interfaced by RS232 to a PC, was placed into the bread crumb at a depth of 22 mm in axial position in order to measure the temperature. Samples were extracted at different final baking temperatures as follows: 60, 65, 70, 75, 77, 80, 85, 90, 95, 98 °C. Crumb samples (about 60 mg) were immediately collected close to the thermocouple and placed into small aluminium DSC pans (150 μL), which were then sealed and dipped in a liquid ice bath to stop baking and, therefore, starch gelatinization. As a result, different degrees of baking and extents of gelatinization occurred and were then determined.

In order to evaluate the extent of gelatinization, the samples were subjected to thermal scanning from 28 to 120 °C at 5 °C/min in a Mettler DSC 20 differential scanning calorimeter (Pabisch Srl, Milano, Italy). An empty cell was used as a reference. The tests were performed in triplicate using the bread crumb baked for different times. Thirty tests were carried out on the raw dough.

The determination of starch gelatinization kinetics was carried out on averaged DSC traces, suitably smoothed, standardized, and deconvoluted according to the procedure described by Zanoni *et al.* (8). Calorimetric traces were deconvoluted into one or two Gaussian curves as a function of the degree of baking. The deconvoluted peaks were subjected to numerical integration, and the relevant areas were compared with the peak areas relating to the raw product.

The extent of gelatinization α, reached at the end of baking, was calculated according to the following equation:

$$\alpha = 1 - \frac{Q_t}{Q_{max}} \qquad \text{Eqn [5]}$$

where Q_l and Q_{max} are the areas of endothermic peaks for partially baked samples and for the raw dough, respectively.

Model for heat and mass transfer during baking

This model is based on phenomenological hypotheses, equations and boundary conditions reported previously (9,10). One of the limitations of this model was the estimation of some thermophysical properties, such as apparent density, thermal conductivity and thermal diffusivity of the product. The values and mathematical relationships used to model the trend of these thermophysical properties during baking were obtained from literature data and did not take the effect of porosity into account. Another limitation was connected to the fact that the overall heat transfer coefficient was not experimental, but it was calculated from the experimental profiles of surface temperatures. In order to overcome the above limitations, the mathematical model has been revised, although the phenomenological hypothesis and equations of the model have not been changed.

Overall heat transfer coefficient

The value of the overall heat transfer coefficient varies, depending on the product surface as follows:

(a) Sample surface exposed to air. The overall heat transfer coefficient of sample surface exposed to air in the oven depends on convection (h_{conv}) and radiation (h_{irr}) as follows:

$$U = \frac{1}{\dfrac{1}{h_{conv}} + \dfrac{1}{h_{rr}}} \qquad \text{Eqn [6]}$$

The convective heat transfer coefficient was evaluated experimentally (11). The radiation coefficient was calculated considering both the sample and the oven as grey bodies, according to relationships reported in the literature (12):

$$h_{irr} = \sigma \varepsilon_2 \left(\frac{T_1^4 - T_2^4}{T_1 - T_2} \right) \qquad \text{Eqn [7]}$$

where:
h_{irr} = radial heat transfer coefficient (W/(m^2·K^4))
σ = Stephan–Boltzman constant (W/(m^2·K^4))
T_2 = temperature of body 2 (K) (i.e. bread surface)
T_1 = temperature of body 1 (K) (i.e. oven wall)
ε_2 = emissivity of body 2 (i.e. bread surface)

(b) Sample surface in contact with the mould. The overall heat transfer coefficient of sample surface in contact with the mould depends on convection (h_{conv}), radiation (h_{irr}) and conduction (h_{cond}), which can be expressed by the following equation:

$$U = \frac{1}{\dfrac{1}{h_{conv}} + \dfrac{1}{h_{rr}} + \dfrac{\Delta x}{\lambda}} \qquad \text{Eqn [8]}$$

where:
λ = thermal conductivity (W/(m·K))
Δx = mould thickness (m)

To solve equations (6) and (8), the temperature of oven walls was measured using self-adhesive thermocouples type J (0.5 mm) (Tersid, Milan, Italy), which were attached to the lateral, upper and lower oven walls. The thermocouples were connected to the automatic data acquisition and recording system.

Apparent density and thermal conductivity

The relationships describing the evolution of apparent density (ϱ) and of thermal conductivity (λ) during baking were set up so as to consider not only the water loss, but also the variation in porosity during baking (ε). For the apparent density:

$$\varrho_b = (\varrho_w X_w + \varrho_d(1 - X_w)) - K\varepsilon \qquad \text{Eqn [9]}$$

where:
ϱ_b = apparent density of bread (kg/m^3)
ϱ_w = apparent density of water (kg/m^3)
ϱ_d = apparent density of dry matter (kg/m^3)
X_w = mass fraction of water in bread (kg water/kg product)
ε = porosity (hollow over total volume ratio)
K = constant of proportionality (kg/m^3).

In our case (11), ϱ_w and ϱ_d are 1000 (kg/m^3) and 895 (kg/m^3), respectively; K is 990 (kg/m^3). Mass fraction of water and porosity vary during baking. X_w was calculated from mass transport equations of our model. Considering that, in our case, the sample diameter remained constant during baking, ε was calculated as:

$$\varepsilon = \frac{H_f - H_o}{H_f} \qquad \text{Eqn [10]}$$

where H_0(m) and H_f(m) are the initial height of the sample at time t = 0 and the final height after a time t, i.e. before and during baking, respectively.

The evolution of the sample height (H_f) during baking was measured and represented by the equations reported in **Table 1.**

The variation in the thermal conductivity as a function of the water content and porosity is described by the following equation:

$$\lambda_b = (\lambda_w X_w + \lambda_d(1 - X_w)) - K'\varepsilon \qquad \text{Eqn [11]}$$

Table 1 Data and equations for solving the mathematical model

Sample weight	110 g
Sample radius	36.8 mm
Sample initial height (H_o)	32 mm
Sample initial temperature	24 °C
Sample initial moisture	409.4 g/kg
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/(w.K)
Air temperature in the oven	250 °C
Temperature of upper and lateral walls of the oven	234 °C
Temperature of lower wall of the oven (over electric resistors)	262 °C
Air 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

Sample height variation kinetics with baking time:

for $0 \leq t \leq 600$ s $\quad H_t/H_0 = 0.125\ 10^{-2} t + 1$

for $t > 600$ s $\quad H_t/H_0 = 1.78$

where:

λ_b = thermal conductivity of bread (W/(m·K))

λ_w = thermal conductivity of water (W/(m·K))

λ_d = thermal conductivity of dry matter (W/(m·K))

K' = constant of proportionality (W/(m·K)) In our case (11), λ_w and λ_d are 0.60 and 0.40 W/(m·K), respectively; K is 0.3 W/(m·K). Mass fraction of water and porosity vary during baking, as shown for the apparent density.

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 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 calculated points of 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, i.e. derivatives were replaced with relevant incremental ratios. 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:

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

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

Data and equations necessary to solve this model are reported in **Table 1.**

Kinetic model for starch gelatinization

The model describing the starch gelatinization during baking is reported in a previous work (8). According to this model, the rate of gelatinization can be described by the trend of disappearance of the second peak in the calorimetric trace, as discussed in the Introduction. Gelatinization follows first-order kinetics of the form:

$$(1 - \alpha) = \exp(-kt) \qquad \text{Eqn [12]}$$

where:

α is the extent of gelatinization and t (s) is the time. The rate constant k (s^{-1}) depends on temperature according to the Arrhenius equation ($K_o = 2.8\ 10^{18} s^{-1}$; $E_a = 138$ kJ/mol). This model was solved to predict the extent of gelatinization at each site within the product during baking. This was obtained from the sum of the various extents of gelatinization with respect to each finite time increase Δt. k was calculated at the temperature of a specific site within the product as follows:

$$k_{T(I,J)} = k_o \exp\left(-\frac{E_a}{RT(I,J)}\right) \qquad \text{Eqn [13]}$$

The extent of gelatinization resulting from the specific time interval was calculated and added to that of previous time intervals as follows:

$$\alpha(I,J)_t = 1 - (1 - \alpha\ (I,J)_{t-\Delta t})\exp(-k_{T(I,J)}\Delta t) \qquad \text{Eqn [14]}$$

This model can be applied both to experimental temperature profiles and to temperature profiles calculated at each site within the product 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 $\Delta t = 10$ s); in the latter, Δt is equal to the time interval applied to solve equations of our model (in our case $\Delta t = 0.1$ s).

Results and Discussion

Table 2 shows a comparison between the experimental results obtained from 11 tests and the results calculated by models for heat and mass transfer and starch gelatinization during baking. Samples were collected at a depth of 22 mm in axial position. This was the site within the product representative of the coldest region of the product under our experimental conditions. In this region, the moisture content did not change and, therefore, gelatinization kinetics only depend on time–temperature relationships. The experimental and calculated time necessary to reach the temperature at the above-mentioned point are reported in the second and third columns. The time calculated by the model to reach the same final temperature is reported in the fourth column. It can be observed that the calculated time is not significantly different from the experimental time.

Mean experimental values of the extent of gelatinization (α) are reported in the fifth column. It shows that the experimental error committed during the tests is relatively high, mainly due to the use of very small sample amounts in the DSC calorimeter. As a result, in most cases, the difference between samples is not significant. Moreover, the moment of complete gelatinization cannot be measured precisely; in fact, the measurement inaccuracy amounts to about 2 min.

The extent of gelatinization calculated by our model according to the calculated temperature profile is reported in the sixth column. It can be seen that the kinetic model for gelatinization allows the experimental trend to be predicted adequately.

Table 2 Variation of the extent of starch gelatinization during baking of crumb samples collected at a depth of 22 mm in axial position

Test No.	Temperature measured at 22 mm from surface (°C)	Experimental time (s)[a] $\bar{x}$	Experimental time (s)[a] s_x	Calculated time (s)	Experimental gelatinization extent[a] $\bar{x}$	Experimental gelatinization extent[a] s_x	Calculated gelatinization extent
1	25	0		0	0	0.01a	0
2	60	563	49	554	0.12	0.04b	0.06
3	65	601	55	597	0.08	0.04ab	0.12
4	70	634	55	653	0.30	0.05c	0.24
5	75	688	62	713	0.36	0.05c	0.45
6	77	700	63	740	0.56	0.04d	0.56
7	80	720	65	760	0.76	0.05e	0.65
8	85	763	69	804	0.91	0.04f	0.79
9	90	840	76	908	0.87	0.04ef	0.98
10	95	950	86	1065	0.98	0.04f	1.0
11	98	1086	98	1200	0.99	0.05f	1.0

Products bearing different superscripts are significantly different ($P < 0.05$).

[a] Means ($\bar{x}$) and standard deviations (s_x).

It can be concluded that the overall baking model set up in this work, including both the heat transfer model and the gelatinization rate model, is realistic and reliable.

Conclusions

Three basic conclusions can be drawn as follows:

1. The mathematical model for heat and mass transfer in the crumb is adequate and reliable. It is more appropriate than other models reported in the literature (13,14) because it is based on a more realistic phenomenological hypothesis, and, being more general, it can be applied under various operating conditions of ovens.
2. The mathematical model for gelatinization is adequate and confirms hypotheses by other authors (4,7). Also, it can be applied to dynamic conditions of temperature variation during baking.
3. This is the first work on baking that deals with the combination of a model concerning a chemical-physical transformation of the product (i.e. a critical phenomenon for the quality of the final product) and a model concerning physical phenomena of heat and mass transfer.

Acknowledgements

Research supported by National Council of Italy, special project RAISA, sub-project No 4, paper No 1791.

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