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Coupling between heat and mass transfer and stoehio-kinetic models to bring insight into Maillard reaction kinetics during baking of sponge-cake products

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ABSTRACT

The objective of this work is to present the methodology used to bring insight into interactions between heat and mass transfer phenomena (within the heating product and between the product and its environment) and the extent of Maillard reaction (influenced by the variations of local values of product moisture content, temperature and reactants concentration) during baking of a sponge-cake type bakery product. Therefore, a heat and mass transfer model coupled with a stoehio-kinetic model has been developed. This model aimed at mechanistically inter-relate the level of operating conditions and the initial composition of the bakery products (in terms of reducing sugars and amino-acid contents) with the nature and extent of Maillard reactions occurring during baking. The developed heat and mass transfer model takes into account internal moisture evaporation and vapour migration within the open porosity of the product during heating as well as apparent liquid moisture migration described by Fick's law. Internal heat transfer phenomena were described using Fourier's law and apparent thermal heat conductivity. External heat and mass transfer phenomena taken into account were convective drying, convective and radiative heat transfer for both heating product and baking tray. Concerning the stoehio-kinetic model developed in the present work, attention was paid to the nature of simplifying assumptions made to deal with phenomena of concern. This point is particularly important considering the complex reaction scheme of Maillard reaction which was necessarily reduced to a simplified observable scheme taking into account bibliographical references about the subject and available experimental data about reactivity acquired during the study. The level of physical realism of heat and mass transfer model previously discussed has hence been adapted to the level of complexity of the stoehio-kinetic model.

Keywords: baking, Maillard reaction, modelling, heat and mass transfer

INTRODUCTION

The present work is part of the REACTIAL project "Prediction and control of the appearance or disappearance of reactional markers during food process and conservation" (ANR-06-PNRA-023) supported by the French National Research Agency. The main aim of this project is (i) to develop elements of generic methodology in order to predict and control the chemical reactivity during food processing and storage and (ii) to study interactions between this reactivity and heat and mass transfer phenomena occurring during processing. In this project, the case of Maillard reaction occurring during baking of cereal products has been chosen as one of the case studies. Maillard reaction associated with thermal treatments concern a complex network of different pathways producing a huge number of newly-formed compounds leading to important changes in food flavour, texture and nutritional value with both positive and negative consequences. Despite the number of papers dealing with Maillard reaction (often with one particular part of the whole reactional scheme), very few studies have taken into account both effect of heat and mass transfer phenomena and composition of the product (in terms of chemical species involved) upon nature and extent of Maillard reaction within solid food products undergoing "realistic" heat treatments.

One of the major issues of this work is hence to extract an "apparent reaction scheme" from the complex and exhaustive Maillard reaction scheme. This apparent reaction scheme must be: (1) able to give reliable representation of the real complex reaction scheme associated with Maillard reaction in the case of bakery products (2) coherent with analytical capabilities by isolating so-called chemical markers representative of the extent of Maillard reaction and accessible by experimentation. This apparent scheme has been determined from a bibliographic review of Maillard reactions in cereal products [1, 2] and from baking experiments and

subsequent analysis of products of Maillard reaction in order to identify the main (and neglected) pathways followed by the initial reagents present in the product recipe and experimenting thermal conditions associated with hot air baking experiments. From this apparent reaction scheme, stoehio-kinetic models (so called chemical model) will be developed. These equations will appear as sink- and source-terms in classical heat and mass transfer continuity equations (so called physical model) in order to predict local kinetics of product temperature rise and moisture loss as well as kinetics of variation of concentrations of chemical species appearing in the reaction scheme. A key point is to adapt the level of complexity and physico-chemical realism of both chemical and physical models to be coupled in order to obtain reliable predictions of phenomena of concern.

The aim of this work is to give an overview of the results concerning the prediction of extent of Maillard reaction during sponge cake baking coupled with the prediction of product temperature rise and moisture loss kinetics during baking. Main hypotheses of both physical and chemical models will be given as well as constitutive equations. Preliminary results of validation will also be given.

MATERIALS & METHODS

The sponge cake formula used for this study comprises 25% flour (Moulins Soufflet, Corbeil-Essonnes, France), 25% monohydrate dextrose (IMCD, Saint-Denis, France), 4% palm oil (local market), 1% sodium chloride and 45% pasteurized liquid eggs –Agro-Doubs, Flagey, France). The mixing and forming protocols are detailed in [3]. Baking experiments and associated chemical analyses upon initial reagents and products of Maillard reactions (including vapour products present in the baking atmosphere) were realised using a specifically instrumented electric convective oven presented in [3]. The thermal environment of the baked products within this oven was precisely characterized in terms of convective and radiative heat flux whose homogeneity within the baking surface was checked. Product core and surface temperature as well as overall product moisture contents (with product sampling every 5 min during 30 min of baking) were recorded during four experiments realised at maximum level of ventilation (v_{max}) and at air temperature of 140, 170 and 200°C and at minimum level of ventilation (v_{min}) at 170°C. Specific non-disruptive sampling system was also designed in order to sample products during baking without thermal perturbation in the oven cavity. Oven atmosphere was also continuously extracted from the oven cavity and analysed using dynamic headspace-solid phase microextraction (HS-SPME) and GC-MS system adapted to the present oven from a previous study [4]. Seven Maillard reaction markers were followed during baking (1 measurement every 5 min during 30 min of baking) among which non-volatile markers measured globally within the product (glucose, amino groups and 5-hydroxymethylfurfural HMF) and volatile markers measured in the baking atmosphere (furfural, 2,3-dihydroxy-6-methyl-pyranone or DDMP, acetic and formic acids and HMF), the analysis protocols being described in [1].

RESULTS & DISCUSSION

The apparent reaction scheme and associated chemical markers (species whose concentration can be assessed by experimental measurements) are presented in Fig. 1 and the associated chemical reactions in Tab. 1.

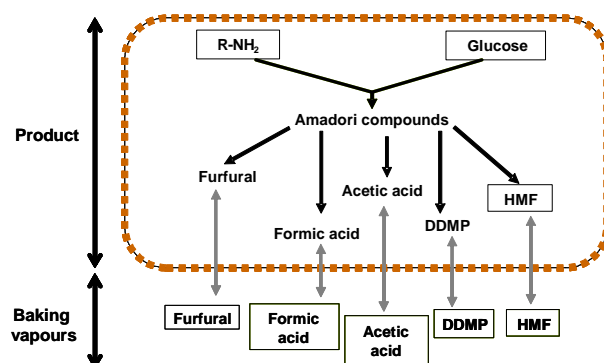


Figure 1 : Apparent reaction scheme for Maillard reactions during sponge-cake baking with chemical markers appearing as surrounded species

Table 1. Chemical reactions used in the apparent reaction scheme of Maillard reaction (R: radical)

Reaction number	Reaction
1	R-NH ₂ + glucose → Amadori compounds + H ₂ O
2	Amadori compounds → R-NH ₂ +HMF
3	Amadori compounds → R-NH ₂ +DDMP
4	Amadori compounds + H ₂ O → R-NH ₂ +Acetic acid + Erythrose
5	Amadori compounds + H ₂ O → R-NH ₂ +Formic acid + 2-deoxyarabinose
6	Amadori compounds → R-NH ₂ +Furfural + 2 H ₂ O + CH ₂ O

In order to convert the system of chemical reactions in Tab. 1 into a stoecho-kinetic model, a partial order of 1 is assumed for all the reaction reagents and the influence of temperature on rate constant k_j of reaction (j) is assumed to be describable by Arrhenius model.

Concerning the modelling of heat and mass transfer phenomena, the cereal product is considered as a biphasic medium constituted of a continuous “pseudo-liquid” phase (L) containing liquid water, dissolved chemical markers of Maillard reaction and dry matter, locally in equilibrium with a gaseous phase (G) composed of vapour and volatile chemical markers. The heat and mass transport phenomena in the product are assumed unidirectional since the lateral surfaces of the mold are thermally insulated. The upper surface of the product is heated by convection and radiation. Neglecting the thermal resistance induced by the very thin mold, the lower surface of the product is heated partly by contact with a perforated baking tray and partly by convection and radiation (part of the lower surface of the mold in contact with baking air). The temperature rise of the baking tray will be also predicted assuming that the baking tray temperature is spatially uniform at all baking times. The value of product porosity is denoted by ϵ (volum fraction of G) and is assumed uniform within the product and constant during baking. The product is assumed non-shrinking during baking, the concentration of dry matter in the liquid phase (in kg of dry matter/ m³ of L) is denoted by β . The porosity of the product is considered as an open porosity allowing gas diffusion from the core of the product to its surface. This mass transport phenomenon is described by a pseudo-Fick law using apparent gas diffusivity D_G (m²/s) taken equal, for all species, to the vapour diffusivity in air. Diffusion of chemical species in liquid phase is assumed negligible except for water where pseudo-Fick law is used with an apparent liquid water diffusivity D_{wL} whose value is taken equal to 10⁻¹⁰ m²/s as a first approximation. In the open porosity of the product and at its surface, the composition of the liquid phase and the gaseous phase in a chemical marker (i) is assumed locally at equilibrium and the values of concentrations in liquid phase C_{iL} (in kg/m³ of L) and in gaseous phase C_{iG} (in kg/m³ of G) are related using partition coefficient K_i :

$$C_{iG} = K_i C_{iL} \quad (1)$$

The value of partition coefficient is determined for HMF since this species is measured both in the product and in the baking vapours. For other compounds such as DDMP, the value of partition coefficient is fixed *a priori* by comparison with the value of the partition coefficient for HMF taking into account the difference in the boiling point of the pure species. Concerning the volatile chemical markers of the Maillard reaction, they are detected and quantified using dynamic headspace-solid phase microextraction (HS-SPME) and GC-MS system. For a given marker (i), the information given by this analysis is expressed in peak area A_i on a chromatogram and must be converted in gas concentration using a proportionality coefficient P_i quantifying the affinity of the species (i) for the fibre selected for the extraction:

$$C_{i\infty} = A_i / P_i \quad (2)$$

where $C_{i\infty}$ (kg/m³) is the concentration of species (i) in the baking atmosphere. The values of proportionality coefficients for species of concern (HMF, formic and acetic acids, DDMP and furfural) were determined in previous studies [1]. Taking into account previous hypotheses and using gas concentration C_{iG} , liquid concentration C_{iL} or content in dry basis X_{iL} as state variable for the species of concern, the gaseous mass flux for the species (i) at a position x from the lower surface of the product is calculated according to:

$$\dot{m}_{iG} = -\epsilon D_G \frac{\partial C_{iG}}{\partial x} = -\epsilon D_G \frac{\partial (K_i C_{iL})}{\partial x} = -\epsilon D_G \frac{\partial (K_i \beta X_{iL})}{\partial x} \quad (3)$$

where x is the spatial coordinate (m). For vapour flux, the vapour concentration C_{wG} is not related to the liquid water concentration C_{wL} using partition coefficient but using classical water activity formalism

(assuming that the water activity a_w is independent of product temperature and that the perfect gas law is applicable for the gaseous phase):

$$C_{wG} = \frac{P_{wG} M_w}{RT} = a_w (X_{wl}) p_{vsat}(T) \frac{M_w}{RT} \quad (4)$$

where T denotes the local product temperature (K), X_{wL} the moisture content (dry basis), p_{vsat} the saturating vapour pressure (Pa), M_w the water molar mass (kg/mole) and R the universal gas constant (J/mole.K). The moisture liquid mass flux is calculated according:

$$\dot{m}_{wL} = -(1-\varepsilon) D_{wL} \frac{\partial C_{wL}}{\partial x} = -(1-\varepsilon) D_{wL} \frac{\partial(\beta X_{wL})}{\partial x} \quad (5)$$

The mass flux expressions having been defined for each component (water in liquid and gas phase, volatile chemical species in gas phase), conservation equations and associated boundary limits are given. For water, using moisture content X_{wL} and vapour content X_{wG} (in kg/ kg of dry matter) as state variables:

$$\frac{\partial}{\partial t} [(1-\varepsilon)\beta (X_{wL} + X_{wG})] + \frac{\partial}{\partial x} (\dot{m}_{wL} + \dot{m}_{wG}) = \sum_j r_{wj} \quad (6)$$

where r_{wj} is the net conversion rate of water (in kg /m³ of product *per* s) for the j^{th} reaction of the reaction scheme presented in Fig. 1. This reaction rate can be zero if water is neither a reactive nor a product of a reaction but can appear as a reaction reagent or product as given in Tab. 1. The associated boundary conditions are :

$$\dot{m}_{wL} + \dot{m}_{wG} = 0 \quad \text{in } x=0, \forall t \quad \text{and} \quad \dot{m}_{wL} + \dot{m}_{wG} = k_m (C_{wG} - C_{v\infty}) \quad \text{in } x=e, \forall t \quad (7)$$

where e is the thickness of the product assumed constant (m), k_m is the external mass transfer coefficient (m/s) and $C_{v\infty}$ (kg/m³) is the vapour concentration in the baking atmosphere (assessed by experimental measurement). For the volatile chemical species, the conservation equation and corresponding boundary conditions are:

$$\frac{\partial}{\partial t} [(1-\varepsilon)\beta (X_{iL} + X_{iG})] + \frac{\partial}{\partial x} (\dot{m}_{iG}) = \sum_j r_{ij} \quad (8)$$

$$\dot{m}_{iG} = 0 \quad \text{in } x=0, \forall t \quad \text{and} \quad \dot{m}_{iG} = k_m (C_{iG} - C_{i\infty}) \quad \text{in } x=e, \forall t \quad (9)$$

where $C_{i\infty}$ is the concentration of volatile compound (i) in the baking atmosphere (kg/m³), noting that the external mass transfer coefficient for species (i) is assumed equal to external mass transfer coefficient used for water. For the non volatile compounds, the conservation equation is simplified since there is no vapour concentration and no migration phenomena for these species. Finally, the enthalpy conservation equation is given as follows:

$$\frac{\partial}{\partial t} [(1-\varepsilon)\beta \hat{H}] + \frac{\partial}{\partial x} (\dot{H}) = 0 \quad (10)$$

where the mass enthalpy (J/kg) and the enthalpy flux (W/m²) are respectively calculated according to:

$$\hat{H} = (c_{pDM} + c_{pwL} X_{wL} + c_{pwG} X_{wG})(T - 273) + \Delta H_{v0} X_{wG} \quad (11)$$

$$\dot{H} = -\lambda \frac{\partial T}{\partial x} + \dot{m}_{wL} c_{pwL} (T - 273) + \dot{m}_{wG} (\Delta H_{v0} + c_{pwG} (T - 273)) \quad (12)$$

where, in Eqs. 11 and 12, c_{pDM} , c_{pwL} and c_{pwG} are the heat capacities (J/kg.K) of dry matter, liquid water and vapour, T the product temperature (K), ΔH_{v0} the latent heat of vapourization for water at 0°C (J/kg) and λ the product apparent conductivity (W/m.K). Note that the enthalpy flux associated with migration of volatile chemical species has been assumed negligible. The corresponding boundary equations are :

$$\dot{H} = \alpha (h_{cv} + h_{ray})(T_{\infty} - T) + (1-\alpha) h_{ct} (T_{ray} - T) \quad \text{in } x=0, \forall t \quad (13)$$

$$\dot{H} = (h_{cv} + h_{ray})(T_{\infty} - T) + \dot{m}_{wG} (\Delta H_{v0} + c_{pwG} (T - 273)) \quad \text{in } x=e, \forall t \quad (14)$$

where α is the surface fraction of the product mold area in contact with baking air through the perforated baking tray and $(1 - \alpha)$ the surface fraction of the product mold in physical contact with the baking tray at the temperature T_{tray} (see discussion and hypotheses above), h_{cv} and h_{ray} are respectively the convective and equivalent radiative external heat transfer coefficients and T_{∞} the temperature of the air assumed equal to the temperature of the radiating walls of the oven.

The predictions of the model are compared with the results of experiments described in the “Materials and methods” section of this document. A first level of validation can be made by considering the prediction of product physical variables such as product centre and surface temperature. For the baking experiment conducted at 170°C and at maximum ventilation, the predictions of the model seem in good accordance with the experimental measurements (Fig. 2).

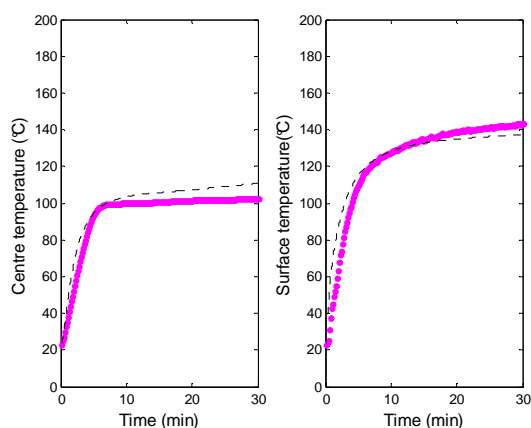


Figure 2 : Comparison between experimental (bold lines) and predicted (dashed lines) product centre and surface temperature during an experiment conducted at 170°C (maximum ventilation)

Concerning the chemical model, data about kinetic parameters for the apparent reactional scheme chosen for this study can not be found. A lack of data has also been noted for equilibrium data concerning the volatile chemical species appearing in the reactional scheme: partition coefficient for the equilibrium between liquid and gaseous phase (inside the product and at the immediate vicinity of its surface) and proportionality coefficient between the gaseous phase and the surface of the fibre used for the HS-SPME measurements. For this reason, a trial and error methodology has been adopted to find acceptable values for the kinetic parameters appearing in the stoehio-kinetic model. These values are given in the Tab.2 and must be considered as rough estimates (and hence used in extrapolation with caution) taking into account the numerous hypotheses made when developing the physical and chemical models and the lack of data in the literature for the model unknown parameters as discussed above.

Table 2. Chemical reactions used in the apparent reaction scheme of Maillard reactions

Reaction number	Pre-exponential factor	Activation energy (kJ/mole)
1	$3.10^{-7} M^{-1}.s^{-1}$	75
2	$5.10^{-6} s^{-1}$	100
3	$5.10^{-6} s^{-1}$	90
4	$6.10^{-10} s^{-1}$	15
5	$9.10^{-10} s^{-1}$	40
6	$7.10^{-8} s^{-1}$	50

When using the kinetic parameters given in Tab.2 and plotting experimental measurements *versus* predicted values for a baking experiment at 170°C realised in triplicate (Fig. 3), an acceptable accordance is found

except for glucose where the model overestimates the values of glucose concentrations within the product. This can be explained by a neglected pathway in the apparent reactional scheme retained for this study and leading to glucose consumption and not taken into account in previous calculations.

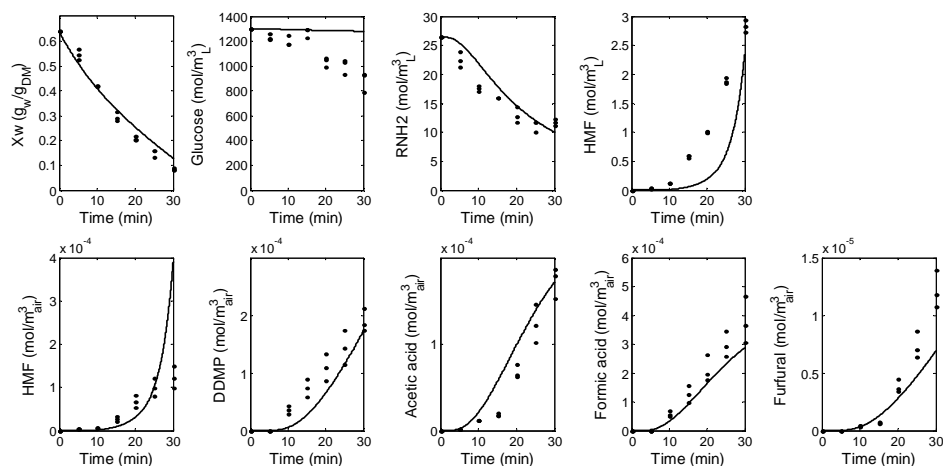


Figure 3 : Comparison between experimental (markers, 3 replicates) and predicted (continuous lines) concentrations for water and chemical species of the apparent reaction scheme during a baking trial at 170°C (maximum ventilation)

CONCLUSION

This work presents an attempt to predict mechanistically the extent of Maillard reaction during baking of a sponge-cake type bakery product. The formalisation of transfer phenomena includes heat and mass transfer phenomena within the product during baking but also transfer phenomena between volatile chemical species and the fibre used in HS-SPME measurements in order to quantify the amount of volatile compounds generated during baking. The complexity of phenomena taken into account and the lack of literature data about unknown model parameters force us to fix the optimal values of unknown kinetic parameters using a trial and error methodology. Although the resulting model predicts experimental measurements to some extent, the values of identified kinetic parameters must nevertheless be used with caution in extrapolated conditions

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