

# Instrumentation of a semi-industrial oven to monitor non-enzymatic browning kinetics during baking

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## ABSTRACT

A semi-industrial convective oven was designed and characterized in this study to monitor the kinetics of thermal reactions like Maillard and caramelization reactions occurring during baking. The thermal environment was characterized by measuring the heat fluxes received by the surface of the cakes under different temperature (140, 170 and 200°C) and ventilation (min, max) conditions. Excellent reproducibility of the convective heat transfer coefficient was obtained from one baking operation to another and the heat fluxes were shown to be uniform on the whole baking floor. Temperature and air humidity sensors were used to observe heat and mass transfers during baking. Besides, the oven was equipped with two original sampling devices enabling to acquire synchronous kinetic data on reaction products in the food matrix as well as in the vapors emitted by the product during baking and this, without disturbing the thermal environment. The production of 5-hydroxymethylfurfural (HMF), which was used as an indicator of the development of non-enzymatic browning, was thus monitored synchronously in the sponge cake and vapors. A good reproducibility of the reaction development was obtained with maximum 8.7 % variations of HMF concentration at all sampling times of independent baking operations. Furthermore, the volatilization of Maillard products in the oven chamber was proved to be proportional to the load of sponge cake being baked, showing the relevance of observing thermal reactions in the baking vapors. This oven should be of precious help for further kinetic modeling of complex thermal reactions occurring in solid food matrix baked under real process conditions.

*Keywords: baking oven; Maillard and caramelization reactions; heat fluxes; HMF*

## INTRODUCTION

Most of the work devoted to Maillard reaction in food deals with elucidating the reaction mechanisms and developing analytical equipment for isolation and characterisation of Maillard reaction products while far less research is being carried out on the evaluation of processing parameters on the Maillard reaction [1]. Besides, many studies concern heat and mass transfers during baking but very few of them consider this transformation operation as a reaction [2]. So, numerous works have described the thermodynamics of food products transformation, but the coupling with the chemical reactions and their kinetic has been neglected. This is probably, among other reasons, because it pre-supposes the development of specific reactors giving access to data on both influencing physical variables and chemical reaction markers. Furthermore, a large number of data are available on the Maillard reaction but for liquid model solutions. These measurements were most often acquired in ideal operating conditions (diluted and agitated liquid environment, under uniform and controlled temperature, water activity and pH) far away from the real processing conditions [3, 4]. Such data appear to be difficult to extrapolate to real solid and heterogeneous food matrices. Finally, the kinetic study of complex reactions like non-enzymatic browning (Maillard reaction, caramelization) is complicated by the profusion of the reactions, their interactions and the nature of the reactants coming from various ingredients. Multiresponse modelling can provide an efficient tool for unravelling complex reaction mechanisms and has been successfully applied for Maillard reaction [5] or caramelization [6].

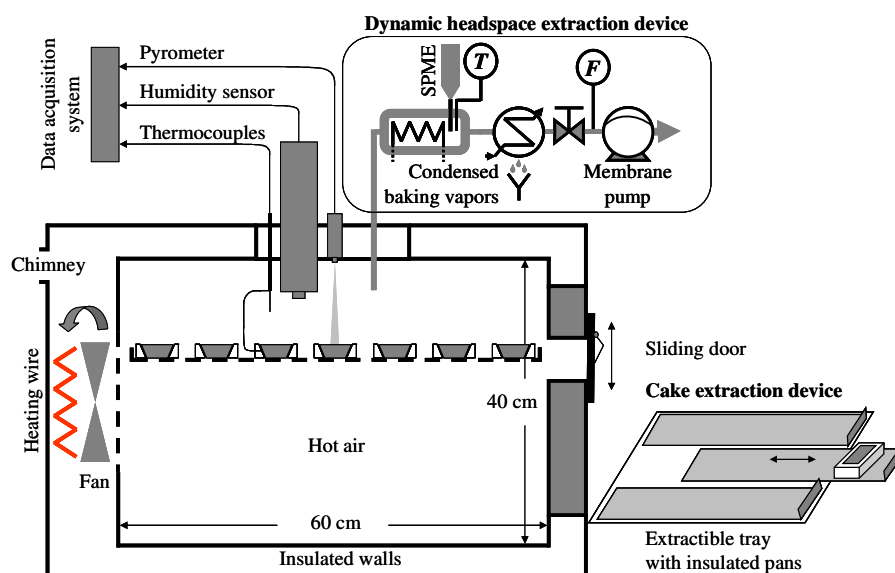
The objective of this work was to design and characterize an experimental device enabling to generate reliable kinetic data on thermal reactions occurring during the transformation of bakery products under real processing conditions. A semi-industrial baking oven was thus developed with the objective of controlling heat transfers, which is a determining parameter of baking process. Sponge cake was used as a model of solid matrix with complex composition and structure evolving during baking. Such an oven was expected to deliver synchronous information on the physical and chemical transformations of the sponge cake during

baking. In this study, 5-hydroxymethylfurfural (HMF) was used as a specific chemical indicator of both Maillard and caramelization reactions.

## MATERIALS & METHODS

*Sponge cake preparation:* the dough was composed of 25% flour, 25% monohydrate dextrose, 4% palm oil, 1% sodium chloride, and 45% pasteurized liquid eggs. The mixing operation is fully described in [7]. Dough batches of 500 g were used to fill 21 rectangular aluminum pans with 20 g of batter, corresponding to an occupation ratio of  $4.375 \text{ kg}\cdot\text{m}^{-3}$  in the oven. The lateral surfaces of the pans were thermally insulated with a 1 cm thick calcium silicate shell (Sored, Messein, France) to ensure a one-dimensional conductive heat transfer from bottom and upper surface of the cake in addition to the convective heat transfer from the top. After sampling, the cakes were immediately cooled down before freezing for further analysis.

*Baking oven:* a static convective batch type oven (Bongard, Wolfisheim, France) of 96 L working volume was equipped with electrical resistances of 7.5 kW power, generating ambient temperatures of up to  $300^\circ\text{C}$  (figure 1). Exceptional thermal homogeneity was achieved through symmetrical insulation of the walls, including the door. A frequency variation system (25 to 50 Hz) was adapted on the ventilation allowing modifications to the convection level. The air was permanently re-circulated inside the oven and partially renewed using an opening located at the bottom of the oven. Baking trays were only located at one level of the oven height. It provided for baking pans on three parallel, removable trays, each containing seven pans.



**Figure 1.** Schematic representation of the instrumented oven equipped with two original sampling devices

*Oven instrumentation:* various parameters were continuously recorded during each baking operation, like core and surface temperature of the cakes, air temperature and air humidity. Radiative and convective heat fluxes at the surface of the cake were recorded during independent experiments in order to characterize the thermal environment of the baking cavity.

The *core temperature* was measured using K-type thermocouples (TC S.A, Dardilly, France): 0.5 mm  $\varnothing$ , 1.5 m length, stainless steel sheath 0.05 mm thick, response time 0.15 s in still air and  $\pm 0.5^\circ\text{C}$  accuracy. The *surface temperature* was measured using an infrared thermometer (Optris CT GmbH, Germany). This instrument ( $-40$  to  $900^\circ\text{C}$ , accuracy  $\pm 1^\circ\text{C}$ ) was fixed on the top of the oven at a distance of 20 cm from the sample surface, giving a 10 mm spot diameter. It was equipped with a cooling jacket protecting the measuring cell from hot environment. The *air temperature* in the oven was measured with T-type thermocouples (TC S.A, Dardilly, France): 1 mm  $\varnothing$ , 1 m length, stainless steel sheath 0.1 mm thick and response time of 0.15 s in still air.

Air humidity in the oven was measured using a Hygrox-C2 humidity sensor (McQueen Cairns International, USA) specially designed for high temperature conditions and which response is proportional to oxygen percentage in the air [8]. The time-air humidity data acquisitions obtained for three independent baking experiments at 170°C with maximum ventilation gave an excellent reproducibility of 4%.

The *heat fluxes* received by the surface of the product were measured using two types of heat flux sensors (Captec, Lille, France): a) an aluminized sensor with an emissivity value close to zero (0.05) allowing the radiation contribution to be neglected, was used to measure the convective flux density ( $\Phi_{conv}$ ) and b) a black sensor with an emissivity value close to one (0.98) was used to measure the total heat flux ( $\Phi_{total}$ ) i.e. convective plus radiative. Both sensors were fixed on top of the surface of an aluminum block that acted as a heat sink. The temperature of the sensors ( $T_{sensor}$ ) and the temperature of the air around them were monitored by means of T-type thermocouples ( $\varnothing$  1 mm; TC S.A., France). In addition to the convective surface heat flux, two other variables could be extracted from the flux measurements: the radiative surface heat flux  $\Phi_{rad}$  ( $W.m^{-2}$ ) using Eq. 1 and the convective heat transfer coefficient  $h_{conv}$  ( $W.m^{-2}.K^{-1}$ ) using Eq. 2:

$$\Phi_{rad} = \Phi_{total} - \Phi_{conv} \quad (1) \quad \text{and} \quad h_{conv} = \frac{\Phi_{conv}}{T_{air} - T_{sensor}} \quad (2)$$

The convection heat transfer coefficient  $h_{conv}$  remained very stable with a mean relative standard deviation of  $\pm 2\%$  during acquisition time. Flux mapping was carried out at 140°C with maximum ventilation with a meshing of nine positions of the flux sensor (three in each tray). Mapping reproducibility was estimated from six independent replicates of the central position at 140°C and relative standard deviations of reproducibility of 6.5%, 5.5% and 3.0% were found for  $\Phi_{conv}$ ,  $\Phi_{total}$  and  $h_{conv}$  respectively. The heat fluxes were measured at three temperature set-points (140°C, 170°C and 200°C) and two convection levels (frequency converter of the fan: 25 Hz and 50 Hz), in the center of the baking area of the empty oven.

The *data acquisition and monitoring system* was a microcomputer with various In/Out loggers: eight channels (FP-AI-110) were available for electrical tension from different sensors (humidity sensor, infrared thermometer). Thermocouple signals were recorded on a specific logger with 8 channels (FP-TC-120). The whole system was interfaced by RS232 to a PC and operated by a program created under Labview© (National instrument, le Blanc-Mesnil, France). All stored data were analyzed using classical tabulator software.

Two original *sampling devices* were specifically designed to carry out kinetic studies during baking. The *sponge cake sampler* consisted in three parallel sliding drawers also used for supporting the pans (figure 1); they could be extracted independently through an oculus drilled in the front door of the oven and placed again in their original position after sampling a pan. The sampling procedure lasted 10 s: opening the sliding door after stopping ventilation, pulling a drawer to take a pan, replacing it and closing the door before returning ventilation on. The *vapor sampling device*, adapted from previous studies [9, 10], was based on the dynamic Headspace-Solid Phase Micro-extraction (HS-SPME) of vapors during baking (figure 1). The hot vapors were continuously pumped through an insulated glass inlet to an extraction chamber (temperature  $65 \pm 2^\circ C$ ) where the SPME fiber was placed and removed every 5 min (CAR/PDMS; Supelco, Bellefonte, PA, USA). The extracted gas was then carried through a refrigerated condensation chamber ( $5^\circ C$ ) at a constant flow rate of 5 L/min using a membrane pump (ILMVAC 400172, Fisher Bioblock Scientific, Illkirch, France) equipped with a flow meter (B 73342, Fisher Bioblock Scientific, Illkirch, France). The SPME fiber was analyzed immediately after extraction using GC-MS. Before each baking experiment, the oven was heated at 300°C for 2 h and a complete blank extraction was performed in the clean empty oven prior to the analyses.

*Analytical methods:* the method used for *SPME fiber analysis* was that proposed by [10] and is fully described in [7]. SPME fibers were desorbed into the injector of an HP 6890 gas chromatograph equipped with an MSD 5973 mass detector (Agilent Technologies, Palo Alto, CA USA). 5-hydroxymethylfurfural (HMF) measurements were performed using a Gilson 321 HPLC apparatus (Roissy-en-France, France) with a C18 column (Supelcosil TM 250 mm x 4.6 mm x 5  $\mu m$ , LC-18-DB) coupled to a UV detector (Waters 996 – Photodiode Array Detector). The extraction solution was 10% Trichloroacetic acid. *Water content* was determined by weighing the sponge cake samples before and after complete desiccation after 24 h in a drying

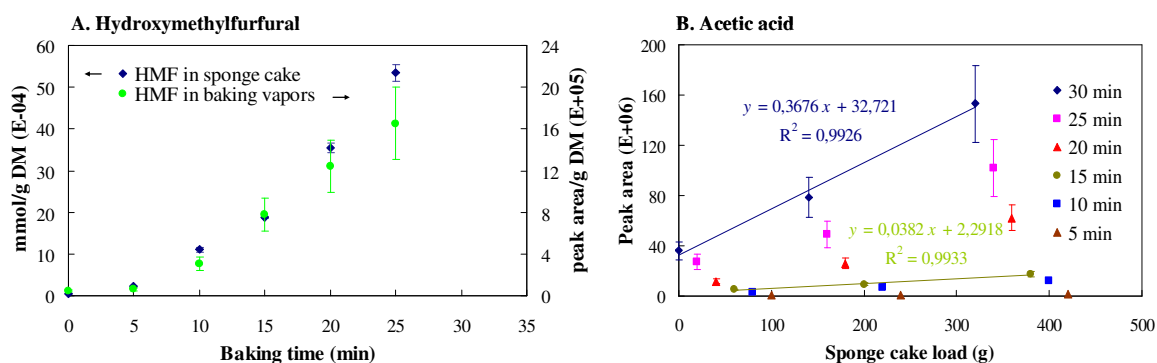
oven (trade Raypa®) set at  $105 \pm 2^\circ\text{C}$ . The weighing was performed using a scale (Mettler Toledo, AB204) with an accuracy of 0.1 mg and a capacity of 220 g.

*Baking experiments* were designed to monitor the development of thermal reactions as well as the internal heat and mass transfers. The oven temperature was set at  $140^\circ\text{C}$ ,  $170^\circ\text{C}$  or  $200^\circ\text{C}$  with two ventilation levels (min, max) at  $170^\circ\text{C}$ ; the total baking time was fixed at 30 min and one cake was sampled every 5 min synchronously to the vapors sampling. The dependent variables monitored during baking were: temperatures (core and surface of the cake and of the air), air humidity, water content, HMF concentration in the cakes and baking vapors. One experiment ( $170^\circ\text{C}$ , maximum convection) was repeated three times to estimate the reproducibility of the baking operation and extent of chemical reaction at all sampling times.

## RESULTS & DISCUSSION

*Monitoring the extent of Maillard and caramelization reactions:* Simultaneous changes to HMF concentrations in the cake and baking vapors at a baking temperature of  $170^\circ\text{C}$ , are represented in figure 2A. After 5 min baking, the concentration of this compound rose very rapidly showing intense production in the cake matrix and volatilization in the oven. Some authors found a different concentration shape against baking time for cookies, because of HMF degradation into other furfurylic compounds taking place at higher temperature ( $300^\circ\text{C}$ ) [9]. The reproducibility of the chemical reactions could be estimated in the matrix and baking vapors by the average standard deviation of the HMF concentration obtained at the different sampling times during a baking experiment performed in triplicate at  $170^\circ\text{C}$  with maximum convection. A reproducibility of 8.7% was achieved in the sponge cake which is very satisfactory and 20.4% in the baking vapors, which corresponds to the reproducibility of the analytical method.

The similarity of HMF production kinetics in the condensed and gas phases tends to prove the relevance of this original approach which consists in monitoring thermal reactions from the volatile compounds emitted during baking. In order to make sure that no saturation of the SPME fiber occurred with the current extraction procedure, two extra loads of sponge cake (100 and 240g) were baked independently at  $170^\circ\text{C}$  and compared to the current load of 420g and the volatile compounds were extracted and analyzed. The chromatographic response had a linear shape ( $R^2 > 0.9$ ) for all compounds and in particular for acetic acid which is presented in figure 2B showing no saturation of the SPME fiber. Thus, despite air extraction for volatile analyzes and air renewal, the conditions prevailing during a baking operation are steady enough to let the composition of the baking vapors be representative of the load being baked.



**Figure 2. A.** Monitoring of HMF concentration during baking at  $170^\circ\text{C}$  in sponge cake and baking vapors **B.** Chromatographic response of volatile acetic acid sampled during the baking of different sponge cake loads at  $170^\circ\text{C}$ .

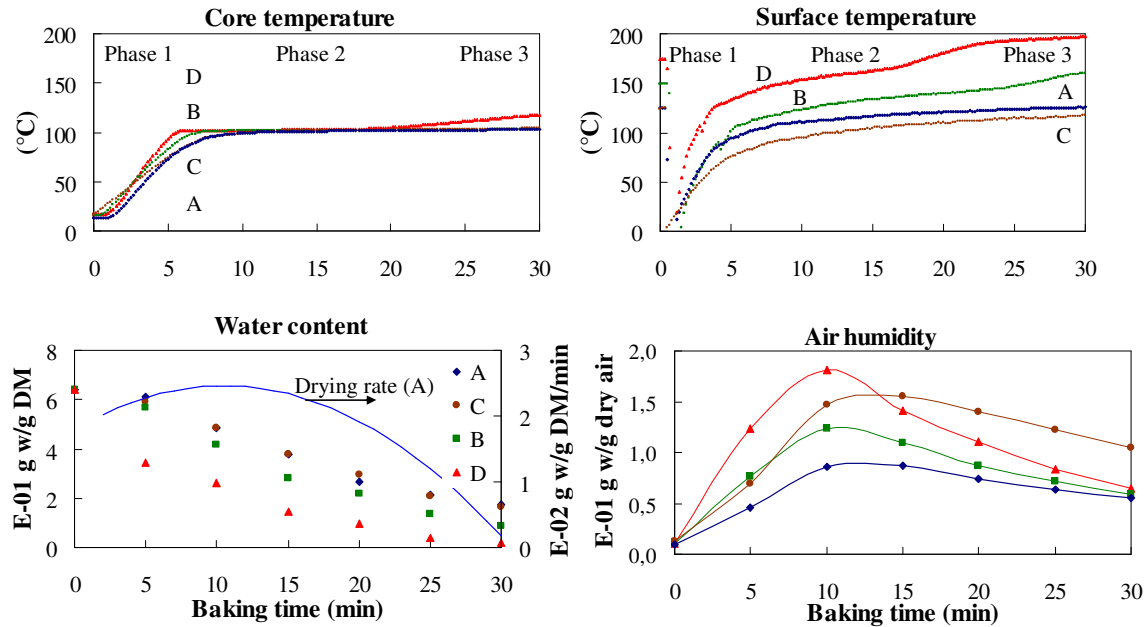
*Monitoring heat transfers in the oven:* in this study, convective and radiative heat fluxes were measured for various purposes: 1/ characterize heat transfers in the oven cavity, 2/ estimate the reproducibility of the thermal conditions, 3/ identify a baking area with uniform heat transfers and 4/ validate the cake sampling device. The convective heat transfer coefficient  $h_{conv}$  was calculated using Eq. 2 and the relative contribution of radiation heat transfer using Eq. 1 for all baking temperature/ventilation settings. The results presented in table 1 show that convection could be characterized by a mean  $h_{conv}$  value of  $40 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$  when ventilation is set at maximum level whatever the temperature; it is lowered to  $26 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$  at minimum ventilation. Radiation accounts for 22 to 42% of the total surface heat flux whatever the ventilation. The reproducibility of the thermal conditions was estimated at 3% using  $h_{conv}$  relative standard deviation obtained for six

independent baking experiments. Heat flux mapping performed at 140°C with maximum ventilation produced an average  $h_{conv}$  spatial dispersion of  $\pm 14\%$  corresponding to  $\pm 5 \text{ W.m}^{-2}.\text{K}^{-1}$ . Considering these results, the surface heat transfers were considered uniform on the whole surface of the baking area. The last purpose of heat fluxes measurements was to make sure that extracting cakes during baking did not disturb the thermal environment. The sampling procedure was repeated 3 times in empty oven set at 140°C with maximum ventilation and the impact on air temperature and heat flux was measured. Even though  $\Phi_{conv}$  and  $h_{conv}$  variables dropped noticeably during 20 s, they were both restored after sampling which was considered as non-disturbing. A full picture of temperature distribution in the oven was given in [11].

**Table 1.** Convection heat transfer coefficient ( $h_c$ ) and relative contribution of the radiative heat flux ( $\Phi_{rad}$ ) to the total surface heat flux ( $\Phi_{total}$ ) at operating conditions.

Baking conditions			$h_{conv}$	$\Phi_{rad} / \Phi_{total}$
Code	Oven temperature (°C)	Ventilation	( $\text{W.m}^{-2}.\text{K}^{-1}$ )	(%)
A	140	Maxi	$40 \pm 5^{(*)}$	21.5
B	170	Maxi	26	34.1
C	170	Mini	36	33.6
D	200	Maxi	38	42.1

(\*) relative error of position (14%) estimated from a meshing of nine positions on the baking floor



**Figure 3.** Evolution of sponge cake core and surface temperatures, sponge cake water content and air humidity during baking at different oven temperature/ventilation settings (A, B, C and D see table 1). The drying rate was calculated using the sliding derivation of the cake water content over two successive times (baking condition A).

*Monitoring heat and water transfers in the sponge cake:* temperature measurements in the core ( $T_{core}$ ) and at the surface ( $T_{surf}$ ) of the sponge cake allowed monitoring internal heat transfer in the product. Product surface temperature, air temperature ( $T_{air}$ ) and air humidity in the oven ( $Y_{air}$ ) can be used to assess evaporative heat transfer at the surface of the cake. Finally, water loss was monitored by weighing a cake sample every 5 min throughout baking. The results obtained for the different temperature/ventilation settings are plotted in figure 3. A first phase lasting around 5 min was characterized by rapid increase in temperature. According to Lostie et al. [12], internal heat transfer is governed by conductive phenomena combined with diffusive water transfer from the core to the surface of the cake. Since air humidity and drying rate immediately start to rise during this first period, it can be concluded that water evaporation and thus latent heat transfer is also involved. The second phase, lasting around 20 min corresponded to a maximum evaporative regime, characterized by a plateau of the core temperature at 100°C, a pseudo plateau of the surface temperature and

a maximum of air humidity and drying rate. Comparable temperature kinetics have been reported in the case of bread [13] and sponge cake [12]. Finally, a third phase lasting 5 to 10 min, could be detected for the highest temperature/ventilation settings C and D:  $T_{core}$  and  $T_{surf}$  increased toward the oven temperature while the drying rate and air humidity decreased. Indeed, evaporation of most of the water caused a final cake temperature increase because of lower latent heat loss.

## CONCLUSION

A semi industrial convective oven was instrumented and equipped with two original sampling devices to study the development of thermal reactions like Maillard and caramelization during baking of a solid food matrix under real process conditions. A proper design of the baking oven provided thermal homogeneity with uniform heat fluxes on the whole surface of the baking floor and maximum variation of  $\pm 14\%$  of the convective heat transfer coefficient ( $h_{conv}$ ). Very satisfactory reproducibility of the baking operations was achieved with  $h_{conv}$  maximum relative variations of 3 %. Such a fine control of the thermal environment in the oven cavity lead to highly reproducible development of non-enzymatic browning reactions: the relative variation of HMF production at different baking times was 8.7%. The two sampling devices specifically developed for this study were proved not to disturb the baking operation and gave access to reproducible kinetic data. The development of Maillard and caramelization reactions could thus be observed synchronously in the cake matrix as well as in the emitted vapors during a complete baking operation under fully controlled thermal conditions. This oven should be of precious help for further kinetic modeling of complex thermal reactions occurring in solid food matrix baked under real process conditions.

## ACKNOWLEDGEMENTS

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