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Monitoring The Kinetics of Non-enzymatic Browning Reactions In Sponge Cake During Baking

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Abstract. *This paper deals with the study of non-enzymatic browning reactions (NEB) in a model sponge cake under controlled baking conditions. Seven molecular markers were measured at different baking times: two reactants, glucose (GLU) and free amino groups (RNH₂), and six reaction products either present in the sponge cake matrix, 5-hydroxymethylfurfural (HMF), or in the baking vapors, HMF, pyranone (PYR), furfural (FUR), formic acid (FA) and acetic acid (AA).*

The baking operation could be divided into three stages: ① moderate chemical reactions while the cake temperature increased rapidly because of heat absorption; ② strong precursor consumption associated to intense evaporation and ③ accelerated production of NEB compounds while evaporation decreased and temperature increased. HMF concentration in the cake matrix was linked to the one in baking vapors which confirmed the interest of monitoring the development of thermal reactions through the baking vapors. Baking temperature had a strong impact on HMF production with 80 time higher amounts after baking 30 min at 200°C versus 140°C. HMF and FUR, both markers of 1,2-enolization pathways presented similar kinetic profiles, with strong accumulation under high temperature and drying conditions. On the contrary, PYR which is a marker of 2,3-enolization seemed to be favored at lower temperatures and higher moisture contents. Finally, the higher amounts of AA compared to FA could indicate the predominance of Maillard reaction versus caramelization during the baking of sponge cake.

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Keywords. Maillard reaction, caramelization, baking oven, HMF, on-line HS SPME extraction.

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Introduction

During baking cereal products are subjected to thermal reactions which contribute to build the final food characteristics. Non-enzymatic browning (NEB) regroups the main reactions playing an important role in the development of flavor, color and even texture of bakery products. However the development of such food properties is linked to the formation of some compounds of safety concern. The dynamic of the scientific research on this issue has brought to light clear needs of deeper knowledge about the reaction mechanisms leading to desired and undesired newly formed compounds or leading to the degradation of valuable compounds.

The two main reactions of NEB, Maillard reaction and caramelization consist of an extremely complex network of reaction pathways which are not yet completely elucidated. Studies on simple model solutions containing carbohydrates and reactive amino groups have been of precious help to gain understanding on reaction mechanisms (Baisier & Labuza 1992, Chen Yang, Chen & Liu 2009, Martins & van Boekel 2005). More knowledge about reaction mechanisms has been produced by multiresponse modeling approaches, most frequently on liquid systems and has led to some relevant parameter estimation and more accurate model predictions (van Boekel 2001). However the kinetic data obtained on simple model solutions cannot easily apply to solid foods: i) because solid foods are complex systems made of numerous reactants delivered by various ingredients, and ii) because the environmental conditions of the chemical reactions can change during the product transformation. It is therefore important to be able to study the NEB reactions of bakery products within their baking environment.

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. It is the initial stage of a multiresponse modeling approach developed for a model sponge cake baked under controlled conditions. Based on a reaction engineering approach, chemical markers were chosen in order to monitor specific pathways of Maillard and caramelization reactions (Fehaili, Rega, Courel, Giampaoli, Brandam, Meyer et al. 2008). The originality of this work relies on one hand on the object of the study which is a solid model food, much more complex and realistic than model solutions and on the other hand on the realistic environment of the chemical reactions provided by an instrumented pilot oven. Special attention was paid to the sampling procedures, designed to generate reliable physical and chemical kinetic data for future modeling.

Material & methods

A pilot oven was specially designed and instrumented to monitor the synchronous variations of physical (temperature, air humidity and product water content) and chemical variables. The two original devices enabling sampling the cake and baking vapors without disturbing the thermal environment are described in detail by Fehaili, Courel, Rega & Giampaoli (2010a).

5 volatile markers were monitored in the baking vapors: 5-hydroxymethylfurfural (HMF), furfural (FUR), 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (pyranone (PYR)), acetic acid (AA) and formic acid (FA). Dynamic Head-Space Solid Phase Micro-Extraction (HS SPME) was used for volatile markers extraction as previously described by Rega, Guerard, Delarue, Maire & Giampaoli (2009). The SPME fibers were then desorbed into an HP 6890 gas chromatograph equipped with an MSD 5973 mass detector (Agilent Technologies, Palo Alto, CA USA).

Glucose (GLU) and HMF were extracted from 1 g of powdered cake or batter suspended in 10 ml of 10% trichloroacetic acid (Sigma-Aldrich, Belfonte). 20 μ L of the filtered supernatant was

then analyzed by HPLC (Fehaili, 2010b). The results were expressed in mmol. kg^{-1} dry matter (DM). HMF analysis was performed using an HPLC system coupled to a UV detector. The results were expressed in mmol.kg^{-1} DM with 8% ($n = 5$) accuracy. Free amino-groups (RNH_2) were analyzed by basic titration following the Sørensen method with an accuracy of 8% ($n = 10$).

The baking experiments were performed at 140 °C (A), 170 °C (B) or 200 °C (C), using maximum ventilation. 21 pans, each filled with 20 g batter were put in the oven for a maximum baking time of 30 min. One pan was sampled every 5 min. and measured for HMF, GLU and R-NH₂. During these 5 min. intervals, an SPME fiber was placed in the baking vapors extraction device and then analyzed for HMF, FUR, PYR, AA and FA.

Results & discussion

The monitoring of physical variables (temperature and humidity) enabled decomposing the baking into three phases (figure 1) (Fehaili et al., 2010a): ① during the first 5 min, the sensible heat transmitted to the cakes resulted in rapid temperature raise with moderate chemical reactions. ② An intense drying took place between 5 to 20 min together with accelerated development of the chemical reactions. ③ During the last 10 min, the drying rate slowed down, the surface temperature increased and advanced non-enzymatic browning products could be observed.

Loss of precursors

Two precursors of Maillard and caramelization reactions were monitored in the sponge cake: GLU which initial concentration was very high since it was chosen as the only sugar ingredient in the cake formula (25 % w/w), and free amino groups (RNH_2) supplied by amino acids, peptides and proteins. Noticeable precursor degradation rate was observed during baking phases ① and ② (figure 1). It then slowed down probably because of advanced product drying that could limit the reagents diffusion. GLU consumptions up to 1.3, 7.7 and 10.0 mmol.g^{-1} DM were achieved at 140, 170 and 200 °C respectively. 4 to 25 times higher loss rate were observed for GLU compared to R-NH₂, which may lead to the following hypotheses: i) other reactions than Maillard reaction were probably involved in glucose degradation like caramelization and sugar isomerization; ii) the amino groups were probably regenerated by Maillard reaction. Martins & van Boekel (2005) and Ajandouz, Desseaux, Tazi & Puigserver (2008) came to the same conclusions when studying the kinetics of NEB reactions in model solutions.

Production of HMF in the sponge cake and baking vapors

HMF is one of the most interesting selected chemical marker: firstly, it is an indicator of both Maillard and caramelization reactions, resulting from the Amadori compound degradation by 1,2-enolization. Secondly, analytical methods were available to monitor this compound in the sponge cake matrix as well as in the baking vapors. And finally, HMF can be *in vivo* converted to 5-sulfoxymethylfurfural which is now considered as a genotoxic compound (Capuano & Fogliano, 2011). The presence of HMF was detected after 5 min baking in both matrix and baking vapors (figure 2). Its accumulation was appreciably accelerated during baking phase ③, resulting in amounts of 48, 594 and 4384 $\text{mg.kg}^{-1} \pm 8 \%$ at 140, 170 and 200 °C resp. Such amounts are comparable to those reported by Ait Ameer et al. (2008) in cookies and Rega et al. (2009) in sponge cake. Strong impact of temperature on HMF production was also observed, in line with the previously cited authors: 80 times higher amounts of HMF were accumulated at 200 °C compared to 140 °C. Similar kinetic profiles were observed in the baking vapors as in the cake matrix. Besides, the chromatographic response of the volatile compounds was proved to

be proportional to the mass of cake being baked (Fehaili et al., 2010a). These results emphasized the interest of monitoring the kinetics of NEB reactions in the baking vapors.

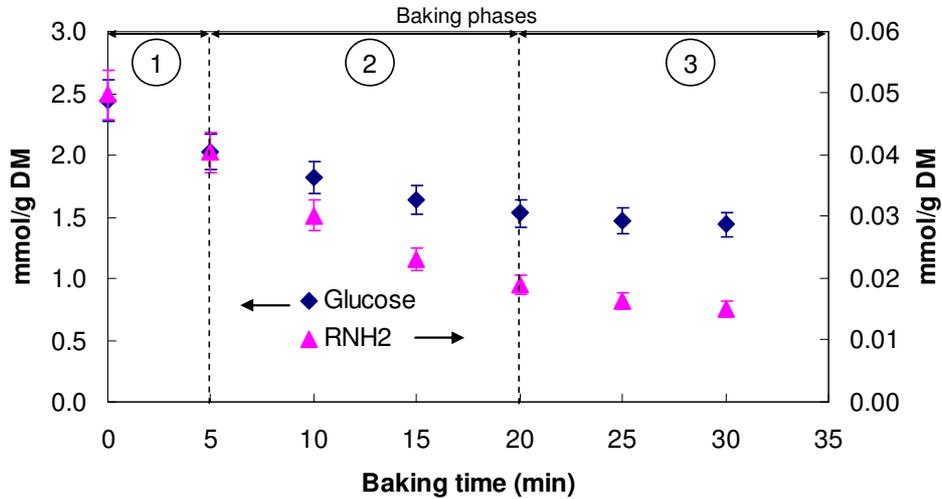


Figure 1. Evolution of Maillard precursors in the sponge cake matrix (baking at 200°C).

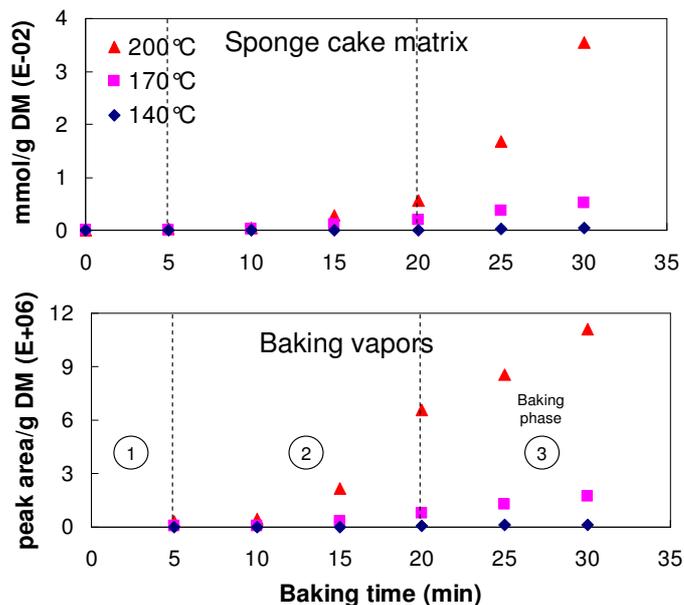


Figure 2. Evolution of HMF content in the cake matrix and baking vapors.

Production of volatile markers

The production of 4 other volatile markers was monitored in the baking vapors and is represented in figure 3 for 200°C baking temperature. Like HMF, FUR is also a marker of 1,2-enolization pathway; it showed a similar kinetic profile to HMF with marked production during baking phase^③. According to Kroh (1994), FUR is mainly produced by pentose degradation. However since no pentose was present in the cake formula, this compound would come from

HMF degradation as reported by Ait Ameer et al. (2008) who worked on cookies at higher baking temperatures.

PYR is an indicator of the 2,3-enolization pathway of Maillard reaction (Davidek, Clety, Devaud, Robert & Blank, 2003). It showed a linear increase throughout baking and appeared earlier than the two previous compounds (figure 3). Indeed, the 2,3-enolization pathway is reported by the previous author to be favored by moderate dehydration conditions, which are indeed prevailing at the beginning of baking and at low baking temperatures.

The formation kinetics of AA and formic FA is represented in figure 3. Since both acids had comparable partition coefficient (Fehaili, 2010b) it appeared that AA was always formed at higher concentrations than FA for all temperature settings. Some authors attributed the higher levels of AA versus FA to the predominance of Maillard reaction versus caramelization (Martins, Marcelis & van Boekel, 2003; Martins & van Boekel, 2005) which might also be the case in this study. Moreover, the production of carboxylic acids goes along with important pH decay: a loss of 2 pH units was observed at 200 °C.

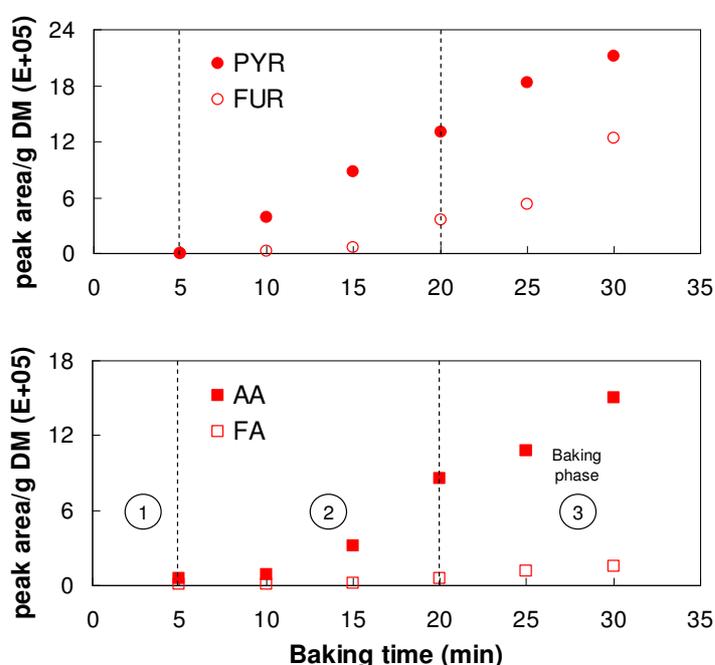


Figure 3. Evolution of volatile reaction products in the baking vapors (baking at 200°C).

Conclusion

The monitoring of selected reaction markers enabled generating kinetic data on the chemical reaction pathways involved in non-enzymatic browning during the baking of sponge cake. The development of Maillard and caramelization reactions could thus be observed in a solid food, with the help of specifically designed experimental tools giving access to the cake matrix as well as the emitted vapors during a complete baking operation under fully controlled thermal conditions. The future implementation of a reaction engineering methodology consisting in coupling heat and mass transfer with stoichiometric modeling of these results should provide more understanding of non-enzymatic browning reactions in bakery products.

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