Analytical Methods

The fate of furfurals and other volatile markers during the baking process of a model cookie

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Abstract

This work investigates the generation and the evolution of some neoformed compounds formed during the baking of a model biscuit. Thank to their physicochemical properties of volatility and hydrophobicity, furfurylic compounds were followed by a double approach: the analysis of the volatile fraction extracted from food matrix and from the vapours released during the thermal process. 5-Hydroxymethylfurfural (HMF) was the main furfurylic compound formed, it followed an exponential kinetic in both the matrix and the vapours of baking biscuits. However, at the very final stage of baking a drop in HMF was observed in the cookie matrix whereas increasing amounts of HMF were still found in the vapours of baking. Moreover, some degradation products of HMF such as furaldehyde (F) and 2-methylfurfural (MF) were also detected. These observations support the hypothesis of a concomitant volatilization and degradation of HMF during the baking of the model cookie, under our experimental conditions.

Monitoring of baking vapours by dynamic SPME coupled to quantitative analysis of chemical and physical markers in the food matrix seems to be a powerful tool to gain knowledge on the behaviour of neoformed compounds generated by thermal processes in solid food systems.

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1. Introduction

During the baking process of cereal products such as bread, cakes and cookies, many textural, physicochemical and organoleptic changes may occur (Sablani, Marcotte, Baik, & Castaigne, 1998). All these cooking-induced changes are important for digestibility and sensorial acceptance by the consumers. The Maillard reaction (MR), caramelisation (CR) and lipid peroxidation (LP) explain most of these changes, although if it is very difficult to characterize the complex mixture of the compounds formed.

Thanks to their high sensitivity to temperature and water activity, furfurals like hydroxymethylfurfural (HMF), furaldehyde (F) and 2-methylfurfural, (MF) have been widely studied as heat treatment indicators and commonly used as baking markers (Ait Ameur, Trystram, & Birlouez-Aragon, 2006; Guerra-Hernandez, Garcia-Villanova, & Ramirez-Jimenez, 2000; Ramírez-Jiménez, García-Villanova, & Guerra-Hernández, 2001). Among them, HMF is considered as a key intermediate in the browning process (Kroh, 1994). HMF may be generated by both MR and CR. In cookies HMF is supposed to be mainly formed by CR, at least when sucrose is used as sugar source (Kroh, 1994). These browning reactions especially take place at the surface of the cookie where the temperature is maximal inducing a strong water evaporation and

sugar crystallisation (Manly, 1998; Swyngedau Chevallier, 1998). In commercial cookies, the HMF content ranges from 0.5 to 74.6 mg kg^{-1} (Ait Ameur et al., 2006), similarly to what is reported for infant cereals (Fernandez-Artigas, Guerra-Hernández, & García-Villanova, 1999; Ramírez-Jiménez, Guerra-Hernandez, & García-Villanova, 2003); in bread and breakfast cereals, the concentrations vary, respectively, between 2.20 and 87.70 mg kg^{-1} (Cardenas Ruiz, Guerra-Hernandez, & García-Villanova, 2004; Ramírez-Jiménez, García-Villanova, & Guerra-Hernandez, 2000; Ramírez-Jiménez, Guerra-Hernandez, & García-Villanova, 2000) and 6.6 and 240.5 mg kg^{-1} depending on the type of cereal flour used (Rufian-Henares, Delgado-Andrade, & Morales, 2006).

Contrary to HMF, 2-furaldehyde (F) and methylfurfural (MF) are mainly produced by pentose degradation (Ledl & Sevrin, 1978). However, they could also be formed by thermal degradation of HMF during CR, as observed by Kroh (1994) in model (aqueous) solutions heated at 300 °C. Despite of being formed at much lower concentrations than HMF, F and MF have also been used as MR markers (Ferrer, Alegria, Farré, Abellan, & Romero, 2002; Kermasha, Goetghebeur, Dumont, & Couture, 1995).

In a previous study on a model cookie submitted to severe baking (300 °C), we observed a significant decrease in HMF after 8 min (Ait Ameur et al., 2006). We could not relate this decrease to any degradation of HMF into F and MF, as only trace amounts of F and MF were detected in the matrix. Consequently we wondered if HMF could volatilize during baking, as furfurals are quite volatile like many MR and CR products. In that case, the kinetics of accumulation of such products could be biased if their concentration is exclusively quantified in the food matrix.

In a recent study on a sponge cake model, Rega, Guerard, Maire, and Giampaoli (2006), developed a method based on dynamic steam-assisted SPME and mass spectrometry in order to follow the release of volatile compounds formed during baking. This ''on-line'' approach allowed monitoring some interesting aroma compounds and markers resulting from both MR and lipid oxidation. The aim of this study was to apply this method to analyse the volatile furfurals collected from vapours during the baking of the model cookie and test the hypothesis of volatilization of HMF. The simultaneous analysis of markers from vapours and matrix as well as the monitoring of some physical parameters during baking could help in understanding the behaviour of neoformed compounds in a processed food product.

2. Materials and methods

2.1. Cookies preparation

Cookies were prepared as described previously (Ait Ameur et al., 2006; Ait Ameur, Mathieu, Lalanne, Trystram, & Birlouez-Aragon, 2007) from wheat flour (60%), hydrogenated palm fat (10%) and sucrose syrup (30%

W/W, stirred at room temperature during 30 min). After mixing the products for 4 min in a bawl (Hobart, USA), the dough was allowed to rest for 30 min in an oven at 25 °C, and was mechanically rolled to reduce the dough thickness to 3 mm. The cookies were baked in a classical home oven (Agroparistech-Massy, France) equipped with temperature sensors and an on-line balance to monitor the weight loss. Baking was processed at 300 °C for a maximal time of 10 min. For kinetic experiments, the cookies were baked in duplicate for increasing times, with a 2 min step, until the final baking time, as previously described (Ait Ameur et al., 2006)

2.2. Monitoring of the volatile compounds during the baking process

The extraction and analysis of volatile compounds were performed by on-line dynamic SPME during the baking of the model cookies following Rega et al. (2006). During the baking of cookies, the hot vapours generated were continuously carried through a glass inlet hood to a refrigerated extraction chamber (pyrex, cone geometry, $V = 40$ mL, $T_0 = 5 \pm 2$ °C) at a constant flow rate of 7.5 L min^{-1}. By passing through the extraction chamber, vapours were continuously sampled by a Stableflex 50/30 μm DVB/CAR/PDMS (Supelco Bellfonte, PA) SPME fibre. Dynamic SPME extraction of volatile compounds was performed during different baking intervals (0–2, 2–4, 4–6, 6–8 and 8–10 min). All samples were immediately analysed in duplicate by GC–MS during two independent baking. Blanks of both fibre and oven backgrounds were systematically done in order to avoid any eventual parasite signal. Moreover, oven pirolysis (4 h at 350 °C) was carried out daily before analysis. SPME fibres were desorbed into a Fisons gas chromatograph equipped with a Trio 1000 mass detector and a DB-Wax column (J&W Science, i.d. 0.32 mm, 30 m, film thickness = 0.5 μm). During GC–MS analysis, the column was held at 40 °C for 5 min, then increased at 5 °C min^{-1} to 240 °C. Helium was used as carrier gas at a linear velocity of 40 cm s^{-1}. The source was kept at 240 °C. The transfer line and the detector were maintained at 250 °C. Mass spectra (EI mode) were generated at 70 eV; they were collected from m/z 29–350, at 3.45 scans s^{-1}. Compounds were identified by standard mass spectra (when available) and by comparison with NIST (Gaithersburg, MD) and INRAMASS (INRA, France) mass spectra. Linear Retention Indices of authentic compounds (when available) or from literature were used to confirm identifications. Table 1 resumes the list of the volatile compounds monitored in vapours of baking and shows the criteria of identification.

2.3. Quantification of furfurals in the cookie

Furfurals were quantified by HPLC–UV according to a recently validated method allowing 98 ± 3% recoveries (Ait Ameur et al., 2006). The ground sample (1 g) was

Table 1
Identified volatile molecules and their m/z used for the identification

Chemical class	LRI[a]	Compound	Method of ID[b]	Fragments[c] (m/z)
Furanic compounds	1450	Furfural	MS + LRI	96, 95, 39, 67
	1560	5-Methylfurfural	MS + LRI	110, 109, 53, 81
	1638	Furfuryl alcohol	MS + LRI	98, 41, 81, 39
	1570	Furan	MS	68, 39, 29
	2461	5-Hydroxymethylfurfural	MS + LRI	97, 126, 41, 69
Ketons	1279	1-Hydroxy-2-propanone	MS	43, 31, 74, 29
	2244	2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)pyran-4-one	MS	43, 144, 101, 55
Aliphatic aldehydes	1377	Nonanal	MS + LRI	57, 98, 43, 41
	1583	Undecanal	MS + LRI	43, 57, 82, 126, 170
	1811	(E,E)-2,4-Decadienal	MS + LRI	81, 41, 67, 152
Acids	1440	Acetic acid	MS + LRI	43, 45, 60

[a] Linear retention index measured on DBWax.
[b] MS + LRI, identified by comparison of mass spectrum and LRI with those of authentic compounds; MS, tentative identification by comparison of mass spectrum with those of mass spectra libraries and by LRI from literature.
[c] Mass spectral data, by order of intensity.

homogenized in water and proteins were precipitated with 2.5 ml 40% (w/v) TCA. The mixture was thoroughly stirred for 5 min and the suspension adjusted to 25 ml with water and centrifuged. Two milliliter aliquot was filtered through a 0.45 μm nylon filter (Waters) and injected on the HPLC system using a C18 Hypersil column (Cluzeau, France) and methanol/sodium acetate (0.04 M) (20/80) as mobile phase. HMF was detected at 284 nm. All analyses were performed in triplicate, including the extraction procedure. The quantification used an external calibration. Results are expressed as mg kg^{-1} dry matter. Preliminary analyses showed that before cookie making, raw materials and sucrose syrup were exempt form furfurals.

2.4. pH measurements in the cookie

To determine the pH in the cookie powder, the AOAC method of measurement of titrable acidity (Ames, Guy, & Kipping, 2001; AOAC, 1990) was applied. Five grams of ground samples were mixed with 20 ml MilliQ water. After stirring for 30 min to obtain a homogeneous mixture, the pH was measured in duplicate on the filtrated solution (IQ240-pH instruments-USA).

2.5. Determination of the water loss and water activity (a_w)

During baking, the water loss can be approximated by the weight loss of cookies. Consequently, water evaporation was determined by weighing the cookies-containing tray, using a balance connected directly to the oven. The quantity of water evaporated corresponds to the difference between the weight at each time and the initial weight, divided by the number of cookies on the tray. The water activity was indirectly measured in the a_w-meter (Thermoconstanter TH2/RTD33 Novasina, Zurich, Switzerland), by quantifying the humidity and multiplying the value observed by 100. The a_w was measured in duplicate at room temperature after controlled cooling.

2.6. Evaluation of the baking level using the fluorescence synchronous spectra (FSS)

The FSS were recorded on a Xenius spectrofluorimeter (SAFAS, Monaco) by scanning the light scattered by Rayleigh diffusion in the 250–600 nm range. Two spectra were recorded for each sample and the mean area (FSSA) of the two dimension spectra was used as browning indicator (CV ⩽ 25%). The FSS of a solid sample allows recovering the photons from the excitation beam which are scattered at the matrix surface (Wu, Partovi, Field, & Rava, 1993). The percentage of photons scattered depends on the physical properties of the sample. A rough dough is characterized by a vitreous structure of light colour associated to maximal light scattering and high FSS, whereas baked cookies develop a more porous and crystalline structure of brown colour, inducing a weak light scattering and a low FSS. The area under the spectrum and the maximal intensity are very well correlated to the time–temperature area measured in the core of the cookie (Ait Ameur et al., 2006). Therefore, the maximal intensity of the fluorescence synchronous spectrum (FSS) was chosen as an indicator of the baking level.

3. Results and discussion

3.1. Evolution of some physical parameters during baking

Fig. 1 shows the evolution of the main physicochemical parameters of cookies at different baking stages. As expected, maximal FSS significantly decreased after 4 min baking in a way correlated with the water content and a_w evolution. Obviously the water content and activity are two essential parameters for the physicochemical structure as well as for the browning reactions. Based on the criteria established by Ait Ameur et al. (2006), standard baking was reached after 6 min, and overcooking (dark brown) was observed at 10 min.
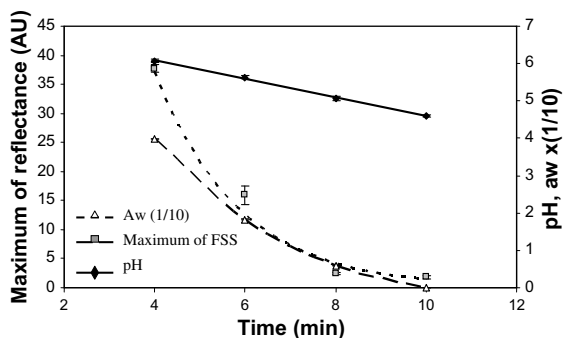
Fig. 1. Evolution of a_w, pH and the maximum of FSS as a function of the baking time.

At the same time, pH fell from 6.1 to 4.6. A pH decrease was already observed in other cereal and starch matrices (Ames et al., 2001), probably as a result of the formation of acidic compounds. In fact, a relatively high amount of acetic acid – a typical Maillard product – was found in the baking vapours during the last minutes of baking.

3.2. Composition of baking vapours

Table 1 shows the main volatile compounds extracted dynamically from the vapours of baking. The evolution of these compounds (grouped in main chemical classes) during the baking of cookie is reported in Fig. 2A. The coefficient of variation varied between 5% and 30% this variation is due to both the reproducibility of baking and dynamic extraction conditions, as the on-line SPME extraction of standard volatile compounds varies from 5% to 24% (data not shown). Furanic compounds and ketons were the most abundant volatiles extracted by the
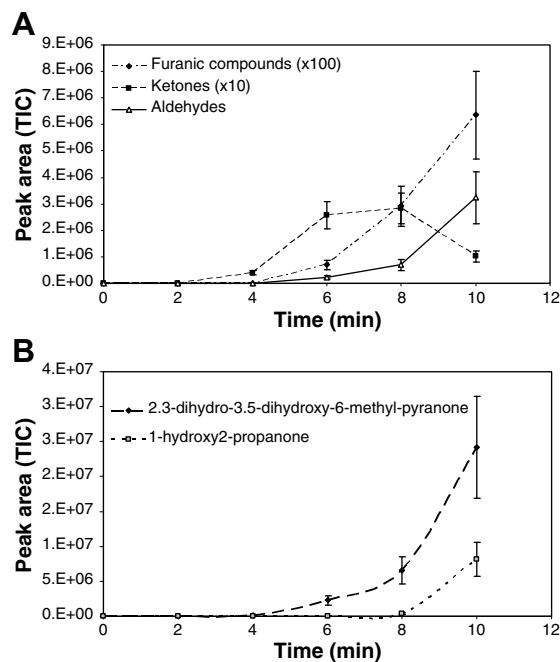

Fig. 2. Recovery of furanic compounds, ketons and aldehydes in vapours generated during the baking of model cookies (300 °C, SPME extraction).

on-line apparatus. These molecules are generated by both sugar and sugar–protein degradation. Furanic compounds exponentially increased after 4 min baking. Their content at the end of baking was 20 and 600-fold higher than ketones and aldehydes, respectively. This family was essentially present as furfurals like HMF, F, and MF. However, furan and furfuryl alcohol were also found in very little amount. Contrary to furfuryl alcohol, furan was mostly detected at the end of baking (6–10 min, data not shown).

The global evolution of ketons in baking vapours was similar to that of furanic compounds: they slowly accumulated during the first minutes of baking and then increased during the two last minutes. Among ketons, two compounds were detected 1-hydroxy-2-propanone and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (DHMP) (Fig. 2B). These compounds are particularly interesting because they are specific markers of CR and MR, respectively. The former mainly results from carbohydrate degradation (Franck & Hofmann, 2000), whereas DHMP is a well known indicator of 2,3-enolization pathway in the MR (Davidek, Clety, Devaud, Robert, & Blank, 2003) as well as a precursor of maltol, a key odorant in cereal products.

Some aliphatic aldehydes were also collected in lower amount than furanic compounds from baking vapours (Fig. 2A). Among them *E,E*-2,4-decadienal and nonanal were the major aldehydes evidenced. These compounds could be formed during lipid peroxidation at the beginning of baking, in agreement with many other studies on other cereal products (Hansen & Schieberle, 2005; Kirchhoff & Schieberle, 2002; Whitfield, Mottram, Brock, puckey, & Salter, 1988). Interestingly, after an early formation during the first minutes, total aldehydes rapidly decreased after 6–8 min baking. This decay could be explained by a further reaction with dough proteins (Beal & Mottram, 1994; Fallico, Arena, & Zappalà, 2003).

3.3. Simultaneous monitoring of furfurals in cookies and baking vapours

Fig. 3 shows the simultaneous evolution of furfurals in the cookie and in vapours collected during the baking process. HMF was the main compound and it was detected after 4 min baking in both matrix and vapours. In the vapours, the increase followed an exponential trend, this result is in agreement with the observations of Rega, Guerard, Delarue, Maire, and Giampaoli (accepted for publication) in a sponge cake system.

Six min baking allowed obtaining a standard cookie as referred FSS, which was similar to that observed in most commercial cookies. However, HMF concentration reached the level of 1100.1 ± 22.4 mg kg^{-1} DM, a concentration 42 times higher than that of commercial cookies. The lower HMF content in commercial cookies is probably the result of lower baking temperatures used in industrial plants (namely between 200 and 250 °C, Ait Ameur et al., 2006). When prolonging the baking process over 8 min, HMF rapidly decreased (Fig. 3). In a previous work we
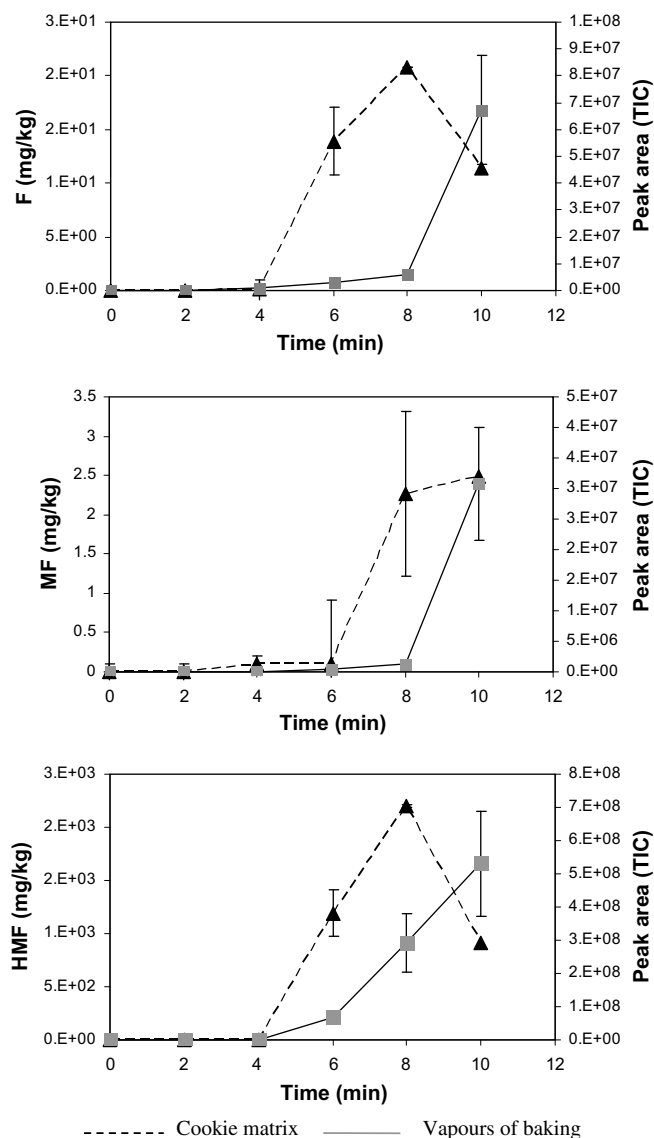
Fig. 3. Evolution of furfurals in food matrix and in vapours of baking of the cookie model.

hypothesised HMF essentially formed from CR (Ait Ameur et al., 2006). At 8 min all the sucrose was already degraded and less than 10% of the resulting glucose and fructose were detected in the matrix. This means that at this baking time a strong transformation of monosaccharides takes place. Considering the low pH reached in the cookie at this late baking stage (4.60 ± 0.02), we suppose that sugar degradation essentially occurs via caramelisation.

The dynamic monitoring of volatiles by SPME showed that despite a decreasing HMF amount in the cookie, this molecule was increasingly released in the vapours until the end of the experiment (Fig. 2). This observation suggests that HMF is still produced at late baking stage and is strongly volatilized from the cookie. The evaporative loss of HMF could also be explained by the dramatic structural changes ongoing in the cookie matrix at severe baking conditions: many breaks and channels could be opened in the cookie structure thus favouring the evaporation rate.

At the same time, the two HMF degradation products, F and MF, were detected in the matrix after 6 min baking in concentrations increasing with baking time but largely lower than HMF. However, they started to be significantly released in the vapours only at the very end (10 min) of the thermal process and at relatively high amount with respect to their concentration in the matrix. This could be explained by their higher hydrophobicity ($\log P_F = 0.448$, $\log P_{MF} = 0.766$) compared to HMF ($\log P = -0.145$) and their higher volatility. In the bread crust which is submitted to a stronger heat impact than cookies, Grosch and Schieberle (1991) found F and MF in much higher concentrations as compared to HMF (at least 10-fold higher). These results support the hypothesis of a thermal degradation of HMF into these two furfurals as proposed by Kroh (1994). On the other hand, the hypothesis proposed by Ledl and Sevrin (1978) of a degradation of pentose into furfurals, seems less pertinent for cereal products where no trace of pentose were found (Ait Ameur et al., 2006). Nevertheless, a second hypothesis cannot be excluded, despite of not being evaluated in this study, which considers that HMF could be consumed by further reactions leading to brown polymers (Kroh, 1994). Actually, HMF is well correlated to browning (Ait Ameur et al., 2006).

4. Conclusions

5-Hydroxymethylfurfural (HMF) is the main compound formed in a model cookie during baking. This compound is formed from sugar degradation, as well as degradation of the Amadori product. Both reactions are favoured at high temperatures and low pH, two conditions obtained during baking of cereal products. This paper shows that HMF is generated in the food matrix and released in the baking vapours with an exponential trend. This molecule is probably involved in the concomitant browning associated to baking. However, the decrease in HMF observed in the matrix under strong baking conditions (10 min at 300 °C) mainly results from its release in the vapour and its further degradation in MF and F. Further hypotheses on the reaction pathways may be raised. As HMF is also a marker of 1,2-enolization pathway in MR, its predominance over DHMP (3×10^8 TIC versus 7×10^6 TIC, after 6 min baking) suggests that 1,2-enolization could be preferred to 2,3-enolization pathway in MR. However, the increasing acidic conditions occurring during baking could also favour CR in the last minutes of baking, as shown by the increasing CR marker 1-hydroxy-2-propanone. Finally, the presence of E,E-2,4-decadienal and nonanal in the baking vapours shows that lipid peroxidation could also occur during the baking of the model cookie.

This work shows the interest of using a combined approach to simultaneously study the volatile and non-volatile fractions of a model cookie to better understand the complex chemical reactions occurring in food during thermal processes. Using an on-line dynamic SPME device combined to an instrumented oven, it is possible to monitor the

release of a large amount of volatile compounds generated during the baking process of a real cereal product. This on-line approach could be applied to other food systems to understand the behaviour of neoformed compounds in a processed food products as it has the advantage not to perturb the development of the food structure nor the thermal reactions occurring during the thermal process of baking.

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