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Comparison of the effects of sucrose and hexose on furfural formation and browning in cookies baked at different temperatures

Lamia Ait Ameur [a], Odile Mathieu [b], Valérie Lalanne [b], Gilles Trystram [b], Ines Birlouez-Aragon [a,*]

[a] *INAPG, Laboratoire de Chimie Analytique, 16 Rue Claude Bernard-75231, Paris Cedex 05, France*
[b] *ENSIA, UMR GenIAL, 1 Avenue des Olympiades, 91744 Massy Cedex, France*

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Abstract

The influence of the type of sugar and baking temperature on sugar degradation, hydroxymethylfurfural (HMF) formation and browning was studied in model cookies. The baking process was characterised by the temperature in the cookie and the water content and activity. A reference browning was selected to compare the differently processed cookies. The accumulation of HMF was modelled at three temperatures for three formulas (sucrose (S-CK), glucose (G-CK) or fructose (F-CK)). HMF started to accumulate at a_w between 0.5 and 0.7 depending on the temperature and followed a first order kinetic, highly dependent on the baking temperature and type of sugar. Cookies baked at 200 °C accumulated 10–100 times less HMF than those baked at higher temperatures. Below 250 °C, S-CK produced less HMF than G- or F-CK, but the inverse was observed at 300 °C.

By simultaneously modelling the kinetics of browning development and HMF formation, rapid comparison of the heat impact on cookies with different formulation and baking process is possible.

Keywords: Browning; HMF; Water activity; Sugars; Cookies

1. Introduction

Baking is a complex process inducing physical, chemical and biochemical changes in the cereal matrix such as volume expansion, evaporation of water, formation of porous structure, denaturation of proteins, starch gelatinisation, crust formation and browning (Sablani, Marcotte, Baik, & Castaigne, 1998). Starch gelatinisation absorbs water, while the development of the Maillard releases water and contributes to the evolution of the dough into crumb (Sablani et al., 1998; Thorvaldsson & Skjoldebrand, 1998). In the specific case of biscuits and cookies, expansion and starch gelatinisation during baking are very limited (Sablani et al., 1998; Sudhakar, Singhal, & Kulkarni, 1995). Consequently, the final water content or the browning are commonly used to determine the end of the baking process (Chevallier, Colonna, & Della Valle, 2000; Ledu, 1966).

Browning is the final result of sugar degradation during baking. The sugars firstly dissolve depending on the amount of water present in the dough, and further crystallise to form an amorphous glass state (Manly, 1998). During the heat treatment sucrose and starch may hydrolyse respectively into glucose and fructose, or a mixture of maltodextrine, maltose and glucose. The newly formed maltose and monosaccharides are reducing sugars which can further participate in the caramelisation and the Maillard reaction when amino-acids are present. According to Kroh (1994), at neutral–basic pH, the former reaction is more rapid than the second one, which is favoured at acidic pH. Both reactions produce brown polymers, which contribute to the surface coloration of the cookies (Manly, 1998; Wade, 1988).

* Corresponding author. Tel.: +33 1 44 08 16 49; fax: +33 1 44 08 16 53.
E-mail addresses: Birlouez@inapg.fr, inesbirlouez@wanadoo.fr (I. Birlouez-Aragon).

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Browning at the surface is generally quantified by the L^*a^*b system, a rapid method directly applied at the surface of the cereal product (Wade, 1988). It is commonly used to control bread baking (Guerra-Hernández, García-Villanova, & Ramírez-Jiménez, 2000; Ramírez-Jiménez, García-Villanova, & Guerra-Hernández, 2001; Zanoni, Peri, & Bruno, 1995) and baby cereals cooking (Ramírez-Jiménez, Guerra-Hernández, & García-Villanova, 2003). Since 1977, Cheftel and Cheftel, proposed to measure the colour at the surface of the biscuits and cookies using the reflectance. Synchronous fluorescence spectroscopy was newly proposed as a method for determining the reflectance spectrum in several cereal flours (Zandomeneghi, 1999).

Very limited information is available on how the physical parameters condition the sugar degradation into HMF and brown polymers. And HMF is considered as a key intermediate in the browning process (Hodge, 1953; Kroh, 1994). The objective of this study was to compare the sugar degradation kinetics during baking at three temperatures of a model cookie formulated with either sucrose, or glucose, or fructose, and to determine the related kinetics of HMF formation and browning of the whole cookie. The results obtained for these different processes are interpreted in relation to the reference baking time.

2. Materials and methods

2.1. Samples

Cookies (CK) were prepared from wheat flour (60%), hydrogenated palm fat (10%) and either sucrose (S-CK), fructose (F-CK) or glucose syrup (G-CK) (30%). After mixing the products for 4 min in a mixer bawl (Hobart N50, Troy, OH, USA), the dough was allowed to rest for 30 min in the oven at 25 °C, and was rolled mechanically to reduce the dough thickness to 3 mm.

The cookies were baked in an oven (SPAG-ENSIA, Massy, France) set at 200, 250 and 300 °C for a maximal time of 15, 12 and 10 min, respectively, to obtain a final comparable surface colour. For kinetic experiments, the cookies were baked for increasing times, with a 2 min step, until the final baking time.

Temperature was measured during baking by sensors placed horizontally in the core of the cookies, and directly connected to a computer to allow online monitoring. Analyses were carried out on the two central cookies of the baking grid, which were associated to the minimal error of baking reproducibility.

Before analysis, the samples were crushed with a professional crusher (Bioblock, Illkirch, France) and stored in glass bottles at −18 °C.

2.2. Moisture and water activity

The water content was measured by the variation of cookie weight during the baking process with a balance (Sartorius-IB 12 EDE-P, France) connected directly to the oven (SPAG-ENSIA, Massy, France).

The water activity was indirectly measured in the aw-meter (Thermoconstanter TH2/RTD33 Novasina, Zurich, Switzerland), by quantifying the humidity and multiplying the value observed by 100. The a_w was measured at ambient temperature after controlled cooling in duplicate for each sample.

2.2.1. Colour measurement

2.2.1.1. L^*a^*b colour system. The colour was measured using a Minolta colour analyser (Minolta, Carrières Sur Seine, France) both at the surface of the cookie and on the powdered sample placed in a small bowl with a cover in order to provide an uniform flat surface. The L^*a^*b colour scale was used but only the L parameter (lightness from 100 for white to 0 for black) was selected as colour index.

2.2.1.2. Fluorescence synchronous spectra (FSS). The synchronous fluorescence spectra were recorded on a Xenius spectrofluorimeter (SAFAS, Monaco) by scanning the emission at similar excitation and emission wavelengths 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.

2.3. Sugar determination

Sugars were quantified on the water–ethanol extract of cookies by HPLC and RI detection according to the method described by Miguez, La Montana Miguélez, and Garcia Queijeiro (2004). The extractant was a 80/20 ethanol (96%) (VWR Prolabo, Fontenay Sous Bois, France)/water solution. The clarifying solutions were composed of 15% potassium ferrocyanide (w/v) (VWR Prolabo, Fontenay Sous Bois, France) (CarrezI) and 30% zinc acetate (w/v) (VWR Prolabo, Fontenay Sous Bois, France) (CarrezII). A standard solution containing glucose (0.01–10.00 g l^{-1}), maltose (0.010–20 g l^{-1}), fructose (0.01–10 g l^{-1}) and sucrose (0.01–10 g l^{-1}) were used for external calibration. The HPLC system (Waters, St-Quentin en-Yvelines, France) was equipped with a NH_2-phase column (5 μm, 250 × 4.6 mm, Machery Nagel, EC 250-4, Nucleosil, carbohydrates, Hoerdt, France) connected to a refractive index detector (RID) (Shimadzu RID-6A). The mobile phase was composed of acetonitrile (VWR Prolabo, Fontenay Sous Bois, France) and water (75:25), the flow rate was 0.8 ml min^{-1}. All analyses were performed in duplicate, including the extraction procedure and expressed as g . 100 g^{-1} of dry matter.

2.4. Furfurals determination

Furfurals were quantified by HPLC-UV according to a method recently validated (Ait Ameur, Trystram, & Birlouez-Aragon, 2006). The ground sample (1 g) was homogenised

in water and HMF extracted by addition of 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 milliliters aliquot were filtered through a 0.45 μm nylon filter (Waters, St-Quentin en-Yvelines, France) and injected on the HPLC system (UVK Lab, Trappes, France) using a C18 Hypersil column (Cluzeau, Sainte-Foy-La-Grande, France) and methanol/sodium acetate (0.04 M) (20/80) as mobile phase. HMF was detected at 280 nm. All analyses were performed in triplicate, including the extraction procedure. Results are expressed as mg kg^{-1} cookie.

2.5. Statistical analysis

The physico-chemical data obtained on the differently processed cookies at the reference baking time were analysed by variance analysis (ANOVA) using Statistica.6. StatSoft Software. Paired *t*-test was also used to compare two formulations or two baking temperatures (the samples were performed in triplicate for each baking temperature).

Kinetic modelling was done on Excel 2003. Microsoft office Software, and the prediction of the reference time was obtained from the polynomial models using MATLAB.7. The MathWorks Inc., Software.

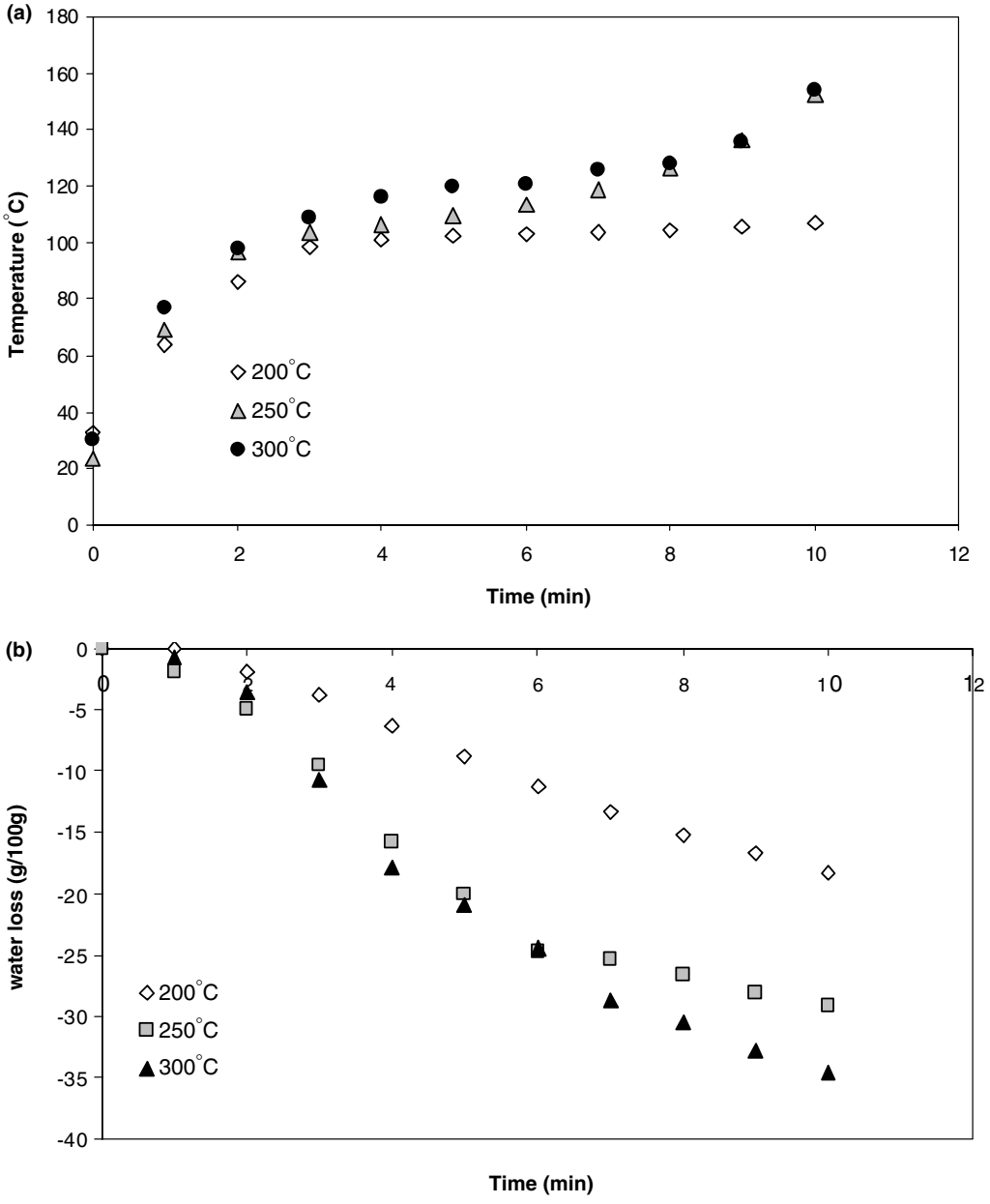

Fig. 1. Evolution of some physical parameters during baking at three oven temperatures. (a) Temperature profile in the core of the cookie. *Note*. The mean SD was: 3.76, 10.73 and 7.32 for the kinetics of 200, 250 and 300 °C, respectively. (b) Water loss during baking at three oven temperatures. *Note*. The mean SD was: 0.00, 6.22 and 0.00 for the kinetics of 200, 250 and 300 °C, respectively.

3. Results and discussion

3.1. Characterisation of the baking process and selection of a reference baking time

In order to compare the sugar degradation and HMF accumulation in cookies baked at various temperatures and with different formulations, it is necessary to define a baking level thanks to an accurate and pertinent indicator. Generally, the temperature in the core of the biscuit is an useful indicator, but in cookies this parameter is not very accurate due to the very low thickness of the product. So, other parameters must be evaluated in parallel, such as the water loss and water activity. However, these two parameters are, respectively, inaccurate and time-consuming. In this study we propose to choose another parameter which is the browning development in the whole ground cookie. Browning is the final step of both the Maillard reaction and caramelisation and one of the end-point of the baking process (Wade, 1988). So we chose as reference the mean browning level measured in commercial cookies. In turn, the kinetics of reflectance in the model cookies allowed determining the reference baking time for each formula and each baking temperatures. The physico-chemical parameters related to the process were then compared at the reference baking time.

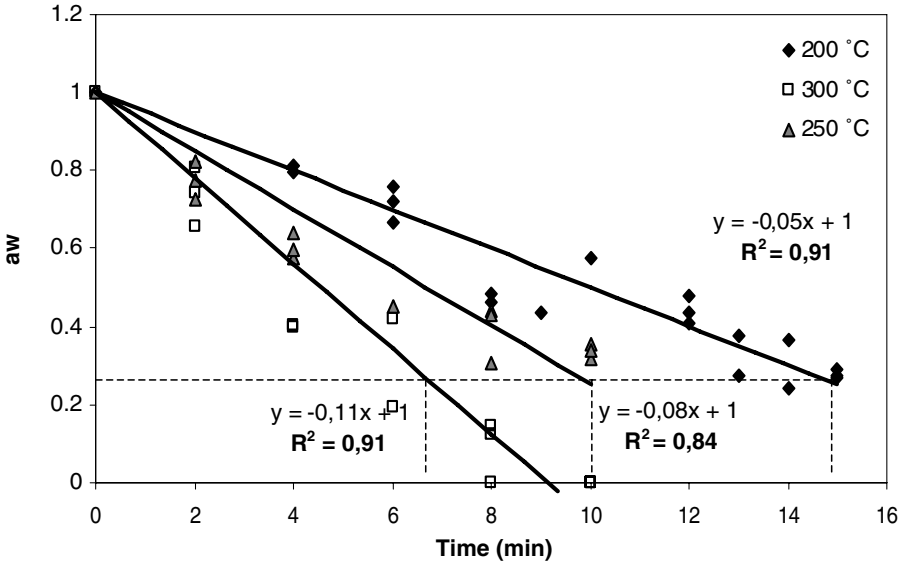

Fig. 2. Evolution of the water activity during baking of S-CK, F-CK and G-CK at different temperatures. *Note*. The reference water activity a_w (0.27 ± 0.10) was determined at the reference baking time as indicated in Section 3.

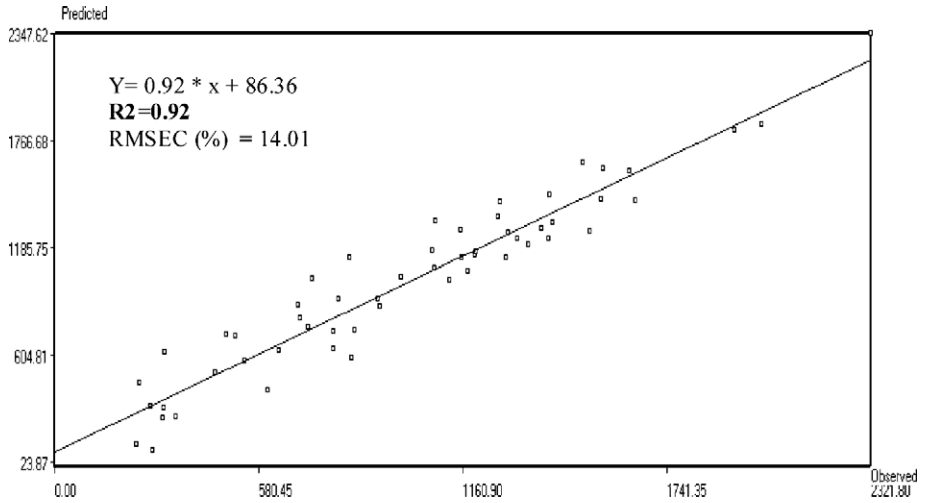

Fig. 3. Prediction of the time/temperature area using the synchronous spectra of S-CK, G-CK and F-CK formulations at different temperatures (PLS regression).

Table 1
Levels of some physico-chemical parameters at the reference baking time for S-CK, G-CK and F-CK baked at different temperatures

		Oven temperature		
		200 °C	250 °C	300 °C
Sucrose	Time (min)	16.4 ± 0.7	10.6 ± 0.4	6.7 ± 0.7
	HC (°C min)	1736.3 ± 37.7	1135.0 ± 86.9	1413.5 ± 120.2
	Water loss (g.100 g^{-1})	−0.20 ± 0.01	−29.79 ± 0.10	−25.21 ± 0.00
	a_w	0.17 ± 0.01	0.37 ± 0.02	0.12 ± 0.02
	HMF (mg kg^{-1})	9.9 ± 0.7	434.5 ± 28.8	1100.1 ± 22.4
Glucose	Time (min)	15.1 ± 0.7	9.4 ± 0.6	6.7 ± 0.9
	HC (°C min)	1582.5 ± 58.7	1411.1 ± 96.2	1308.3 ± 86.7
	Water loss (g 100 g^{-1})	−21.11 ± 0.00	−33.01 ± 0.00	−25.40 ± 0.00
	a_w	0.29 ± 0.00	0.35 ± 0.01	0.25 ± 0.00
	HMF(mg kg^{-1})	34.2 ± 0.8	167.4 ± 3.5	286.7 ± 5.4
Fructose	Time (min)	15.5 ± 0.9	9.2 ± 1.0	6.8 ± 0.9
	HC (°C min)	1528.6 ± 60.4	1290.0 ± 12.2	1211.8 ± 81.6
	Water loss (g 100 g^{-1})	−26.71 ± 0.00	−23.44 ± 0.00	−29.56 ± 0.00
	a_w	0.21 ± 0.00	0.38 ± 0.02	0.29 ± 0.00
	HMF(mg kg^{-1})	39.6 ± 0.5	215.3 ± 0.0	263.4 ± 0.0

Note. The reference baking time was defined as the time predicted from the reference FSSA as measured in commercial cookies (see Section 3).
HC: heat charge evaluated as the time-temperature area.
The results are expressed by the mean value of two repetitions ± the mean of standard deviation.

Table 2
Evolution of the sugar content (in g 100 g^{-1} dry matter) as a function of the baking time

	Cooking time (min)	Sucrose	Maltose	Maltodextrin	Glucose	Fructose
a-Sucrose						
200 °C	4	13.30 ± 0.02	ND	ND	ND	ND
	8	13.80 ± 0.01	ND	ND	ND	ND
	12	13.10 ± 0.02	ND	ND	ND	ND
	14	13.10 ± 0.00	ND	ND	ND	0.10 ± 0.00
	15	13.00 ± 0.00	0.40 ± 0.00	ND	0.30 ± 0.00	0.80 ± 0.00
300 °C	4	13.40 ± 0.07	0.70 ± 0.02	0.90 ± 0.07	ND	ND
	6	13.00 ± 0.65	0.60 ± 0.01	1.20 ± 0.20	0.20 ± 0.02	ND
	8	1.22 ± 0.43	0.60 ± 0.00	1.10 ± 0.01	1.30 ± 0.10	0.10 ± 0.01
	10	0.80 ± 0.59	0.50 ± 0.00	4.80 ± 0.17	0.20 ± 0.17	ND
b-Glucose						
200 °C	4	ND	ND	ND	13.50 ± 0.18	ND
	8	ND	ND	ND	14.50 ± 0.22	ND
	12	ND	ND	ND	13.20 ± 0.15	ND
	14	ND	ND	ND	13.20 ± 0.02	ND
	15	ND	ND	ND	11.90 ± 0.03	ND
300 °C	4	ND	0.50 ± 0.01	0.87 ± 0.11	13.20 ± 0.26	ND
	6	ND	0.60 ± 0.03	1.07 ± 0.11	14.70 ± 0.35	ND
	8	ND	0.60 ± 0.00	1.00 ± 0.11	13.50 ± 0.00	0.10 ± 0.06
	10	ND	0.40 ± 0.02	3.66 ± 0.09	2.80 ± 0.08	ND
c-Fructose						
200 °C	4	ND	ND	ND	ND	14.70 ± 0.03
	6	ND	ND	ND	ND	14.70 ± 0.07
	8	ND	ND	ND	ND	14.60 ± 0.55
	10	ND	ND	ND	ND	14.70 ± 0.35
	12	ND	ND	ND	ND	13.00 ± 0.17
	15	ND	ND	ND	ND	12.00 ± 0.04
300 °C	4	ND	0.80 ± 0.02	1.00 ± 0.01	0.10 ± 0.01	14.50 ± 0.02
	6	ND	0.90 ± 0.00	1.40 ± 0.03	0.10 ± 0.00	14.40 ± 0.13
	8	ND	0.90 ± 0.01	1.60 ± 0.00	0.40 ± 0.00	12.30 ± 0.15
	10	ND	0.70 ± 0.02	4.30 ± 0.03	0.70 ± 0.01	3.10 ± 1.17

ND, not detected.

3.2. Variation of the temperature in the core of the cookie during baking

Fig. 1a shows the increase in the mean temperature in the core of the cookie as a function of the baking temperature. The curves were not significantly influenced by the type of sugar used in the formulation, so the mean curve was constructed. The mean variation coefficient of the temperature quantification at a given baking time varied as follows depending on the oven temperature: 4.43% at 200 °C, 9.71% at 250 °C and 8.04% at 300 °C. At 250 °C and 300 °C, three phases were identified in the temperature curve as expected (Chevallier, Colonna, Buléon, & Della Valle, 2000), while only two phases were observed at 200 °C, confirming previous results (Chevallier et al., 2000). The first phase (0–2 min) is characterised by a rapid increase in the temperature. In the cookie models, the temperature reached 86.6 ± 8.6 °C, 93.6 ± 4.9 °C and 93.9 ± 10.0 °C, at 200, 250 and 300 °C, respectively, with no significant effect of the type of sugar. This rapid increase is essentially due to the water condensation on the cold surface of the cookie at the beginning of baking. The evaporation–condensation is considered as the governing heat transfer mechanism responsible for the temperature rise in the food matrix (Chevallier et al., 2000; Sablani et al., 1998). The second phase is characterised by the stabilisation of the temperature at 103.3 ± 0.5, 112.4 ± 7.5 and 119.7 ± 6.5 °C for the kinetics at 200, 250 and 300 °C, respectively. This phase was much longer at low temperatures (8 min at 200 °C) than at higher temperatures (4 min at 250 and 300 °C), in agreement with Sablani et al. (1998). After 10 min baking, almost all the water

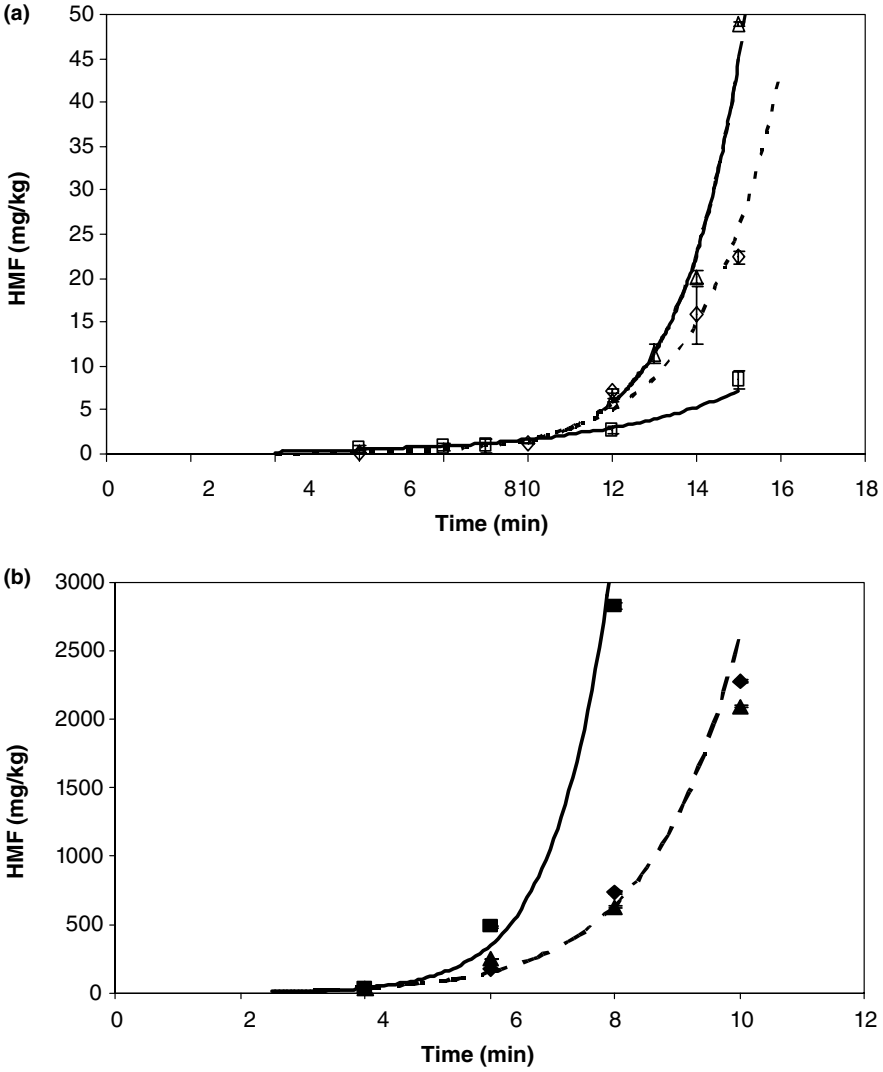

Fig. 4. HMF accumulation during baking in model cookies with different formulations. *Note*. Sucrose (S-CK: square), glucose (G-CK : lozenge) and fructose (F-CK : triangles) baking temperature 200 °C. (a) At an oven temperature of 200 °C. Discontinuous line: exponential fitting curve of G-CK ($y = 0.01\,e0.54x$; $R^2 = 0.98$) and F-CK ($y = 0.0017\,e0.68x$; $R^2 = 0.99$) formulations. Continuous line: exponential fitting curve of S-CK ($y = 0.10\,e0.2875x$; $R^2 = 0.95$) formulation. (b) At an oven temperature of 300 °C. Discontinuous line: exponential fitting curve of G-CK and F-CK formulations ($y = 2.11\,e0.7129x$; $R^2 = 0.99$). Continuous line: exponential fitting curve of S-CK formulation ($y = 0.42\,e1.1224x$; $R^2 = 0.99$).

was evaporated, so that the temperature increased again up to 152.6 ± 34.0 and 158.0 ± 1.3 °C at 250 and 300 °C, respectively, while remaining at 103 °C at 200 °C.

3.3. Moisture profile during baking

The loss of water followed three phases during the baking process (Fig. 1b). After a latency step, a decrease was observed, proportional to the oven temperature (18.33 ± 0.00 mg $100\ g^{-1}$, 29.11 ± 6.22 mg $100\ g^{-1}$ and 34.51 ± 0.00 mg $100\ g^{-1}$ at 200, 250 and 300 °C, respectively), and independent on the type of sugar in the dough, these results are in agreement with the results obtained by (Doescher, Hoseney, Milliken, & Rubenthaler, 1987). The third step is characterised by a stabilisation of the cookie weight. The slight and continuous decrease in the moisture may be related to the very limited expansion and starch gelatinisation of the cookies due to the low initial water content. This profile is similar to that observed in the bread crust, but very different to the crumb, where an increase in the water content appears at the end of the baking process (Sablani et al., 1998).

3.4. Evolution of the water activity during baking

The water activity (a_w) (Fig. 2) decreased linearly as a function of the baking time with a slope proportional to the oven temperature (-0.048 ± 0.017, -0.060 ± 0.034 and $-0.096 \pm 0.006\ min^{-1}$ at 200, 250 and 300 °C, respectively). No significant difference was observed between the different formulations. After 10 min baking, a_w reached 0.452 ± 0.031, 0.336 ± 0.019 and 0.000 ± 0.000 at 200, 250 and 300 °C, respectively. The water activity is considered as a good indicator of the baking process (Cheftel & Cheftel, 1977), but no indication has been proposed to characterise the cookies baking time.

3.5. Colour development

The colour development could be a good way to characterise the baking process, as proposed by Cheftel and Cheftel (1977) and Wade (1988). But the colour at the surface is somewhat heterogeneous and difficult to accurately appreciate. So, we propose to measure the global browning in the whole ground cookie, which is expected to better correlate to the total heat charge absorbed by the dough during baking. Two methods were compared, the L parameter using a colorimeter and the reflectance using synchronous fluorescence spectra. The accuracy and pertinence of these two analysis were deduced from the quality of the correlation to the heat charge determined as the time/temperature integral in the core of the cookie. Fig. 3 shows the much better PLS regression obtained using fluorescence synchronous spectra (FSS) ($R^2 = 0.93$) than using the L parameter ($R^2 = 0.38$) (not showed). FSS area (FSSA) was also well correlated to the water activity ($R^2 = 0.91$). The kinetics of browning development, measured by FSSA, were modelled as polynomial curves for each formulation and baking temperatures with satisfactory correlation coefficients (R^2 between 0.87 and 1.00).

We therefore selected FSSA to monitor the browning development and determine the optimal baking time at different temperatures and for the three formulations. For this purpose, we quantified FSSA in twelve commercial French cookies from different trades and selected the mean FSSA (1068.5 ± 277.5 RU) as the reference browning index. In turn, the reference baking time was determined (Table 1) from the FSSA kinetic models for each process conditions. Reporting this value in the model describing the relationship between a_w and FSSA for each formula, a mean a_w of 0.27 ± 0.10 was obtained (Fig. 2). We confirm that the heat charge is similar (non significantly different) whatever the temperature applied in the oven. But we

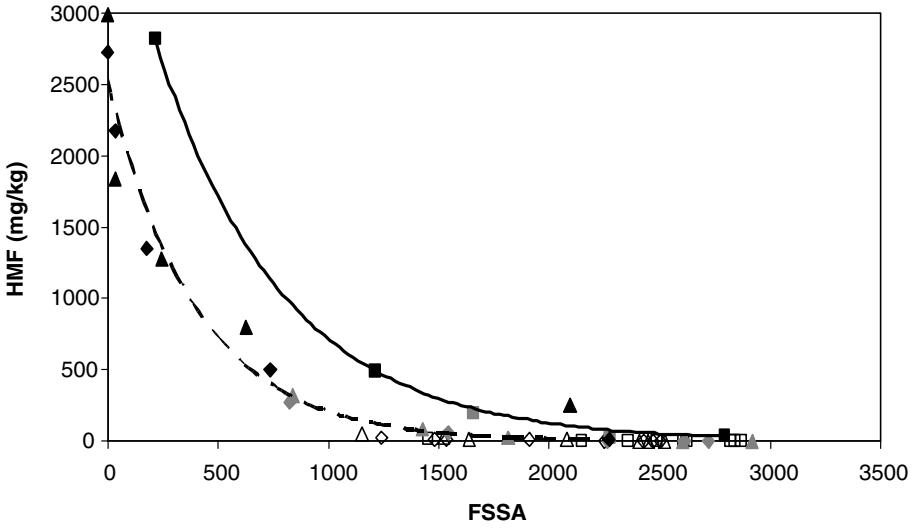

Fig. 5. Relationship between FSSA and HMF in cookies. *Note*. Sucrose (S-CK: square), glucose (G-CK : lozenge) and fructose (F-CK : triangles). Oven temperature 200 °C (open symbols), 250 °C (grey symbols) and 300 °C (black symbols). Discontinuous line : exponential fitting curve of G-CK and F-CK formulations ($y = 2519.2\ e{-}0.0025x$; $R^2 = 0.98$). Continuous line: exponential fitting curve of S-CK formulation ($y = 4089.4\ e{-}0.0017x$; $R^2 = 0.99$).

observe that sucrose-formulated cookies (S-CK) need more baking time to reach a similar browning level than hexose-formulated cookies ($p < 0.005$).

3.6. Sugar degradation and transformation in furfural as a function of sugar type and baking temperature

3.6.1. Sugar degradation during baking

Table 2 reports the evolution of sucrose, fructose and glucose at 200 and 300 °C in the differently formulated cookies as a function of time. At 200 °C no significant change was observed until 8–10 min. Less than 20% hexose and 35% sucrose were degraded after 15 min, near from the reference baking time. Traces of maltose were found at 15 min revealing some starch hydrolysis.

At 300 °C in G-CK and F-CK, hexose began to dramatically decrease after 8 min, whereas sucrose in S-CK drastically decreased after 6 min, near from the reference baking time (7 min). Only trace amounts of glucose and fructose were detected. This suggests that hexose are rapidly degraded, so that sucrose hydrolysis should be the limiting step of the sugar degradation process. Surprisingly, neither glucose, nor fructose were still degraded in G-CK and F-CK at the same baking time. We therefore deduce

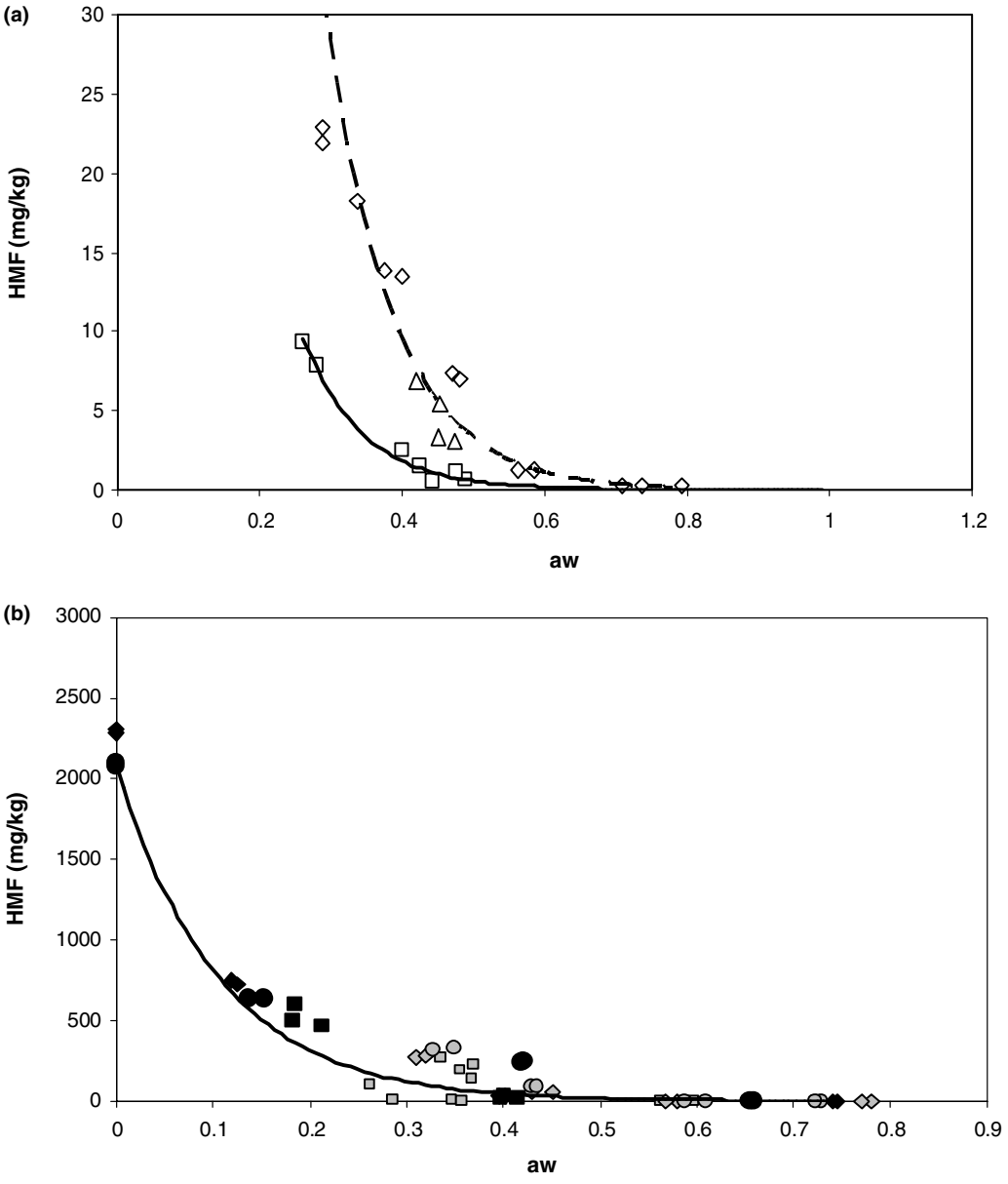

Fig. 6. Relationship between HMF and a_w in cookies. *Note*. Sucrose (S-CK: square), glucose (G-CK : lozenge) and fructose (F-CK : triangles). (a) Oven temperature of 200 °C. Discontinuous line: exponential fitting curve of G-CK and F-CK formulations ($y = 712.47\,e{-}10.78x$; $R^2 = 0.97$). Continuous line: exponential fitting curve of S-CK formulation ($y = 228.4\,e{-}12.128x$ $R^2 = 0.87$). (b) Oven temperature of 250 and 300 °C. Continuous line: exponential fitting curve of S-CK, G-CK and F-CK formulation ($y = 2075.4\,e{-}9.414x$; $R^2 = 0.99$).

that hexose degradation is faster in sucrose containing cookies than in hexose-formulated ones.

Some maltodextrin and maltose were present at 4 min in all cookies indicating that starch is hydrolysed. The amount of maltose (0.5–0.8 g 100 g^{-1} of dry matter) measured in the present cookies are in agreement with the results reported by Fernández-Artigas, Guerra-Hernández, and García–Villanova, 2001. Moreover maltodextrin tended to accumulate with time, but not maltose, nor glucose, suggesting that maltodextrin hydrolysis is the limiting step for the production of glucose from starch. Fructose and glucose degradation profiles in hexose-containing cookies (F-CK and G-CK) were very close, suggesting that the two sugars had similar reactivity upon heat treatment. In S-CK however, almost no fructose was detected while some glucose was, but this could result from the double origin of glucose in those cookies, starch and sucrose.

3.6.2. HMF accumulation

In this study we confirm that HMF production from hexose is very sensitive to the baking temperature and follows a first order kinetic, while only traces of furfurals, such as F and MF are detected (Ait Ameur et al., 2006).

Whatever the oven temperature (and Table 1), F-CK accumulated significantly more HMF than did G-CK. As glucose and fructose were similarly degraded (17.93 and 18.37%, respectively), we can suppose that fructose is more efficiently transformed in HMF than does glucose, confirming the data obtained by Kroh (1994) in dessert wine. This higher conversion of fructose into HMF could be due to a fructose-specific reaction pathway involving a 1,2-endiol intermediate in acidic media (Antonelli, Chinnici, & Masino, 2004; Hodge, 1953; Kroh, 1994; Yeboah, Alli, & Yaylayan, 1999). However, when considering the kinetic models (Fig. 4a), the difference between G-CK and F-CK was only visible at the final baking time.

Under an oven temperature of 300 °C, S-CK were associated to the lowest HMF accumulation rate, and the final HMF concentration at the reference time was 10–100 times lower than those calculated for G-CK and F-CK. At 300 °C however, the inverse was observed, as the highest HMF concentration was found in S-CK (at the reference baking time of 6 min) (Table 1). HMF appeared earlier in S-CK than in hexose containing cookies and with a significantly higher first order rate (Fig. 4b), what is in agreement with the sugar degradation profiles described above.

3.7. HMF evolution as a function of browning and water activity

In Fig. 5 HMF is plotted against FSSA. The exponential models obtained for different temperatures and specific formulations were not significantly different ($R^2 = 0.97$). However, HMF concentrations measured in S-CK were modelled differently than in G-CK and F-CK, who fitted on the same exponential curve ($k = -0.18$, $R^2 = 0.87$ and $k = -0.13$, $R^2 = 0.98$, respectively, where k is the exponential constant). This confirms that sucrose needs more baking time, and therefore a higher heat charge, to produce a similar browning, confirming above results. In that time sucrose was totally hydrolysed, whereas the released hexose produced HMF at a higher rate than did free hexose in G-CK and F-CK.

Table 3
Water activity corresponding to the formation of HMF

a_w	200 °C	250 °C	300 °C
Sucrose	0.42 ± 0.01	0.38 ± 0.10	0.72 ± 0.12
Fructose	0.46 ± 0.02	0.60 ± 0.01	0.66 ± 0.00
Glucose	0.63 ± 0.02	0.57 ± 0.18	0.73 ± 0.12

HMF formation was evaluated as the analytical limit of quantification (3.6 mg kg^{-1})The results are expressed by the mean value of two repetitions ± the mean of standard deviation.

In Fig. 6, HMF is modelled as a function of the water activity. No significant effect of the type of sugar, nor of the temperature was observed above 200 °C, so that one model was designed (Fig. 6b). In contrast at 200 °C, a significantly different model was obtained for hexose and sucrose (Fig. 6a).

HMF is very sensitive to the water activity, as the formation of 1 mole HMF needs the release of 3 moles of water. To better describe the relationship between the water activity and the formation of HMF, we determined the critic a_w value, where HMF began to form. This HMF level was defined as the analytical limit of quantification of 3.60 mg kg^{-1}. The water activity allowing HMF formation was significantly higher at 300 °C (critical a_w of 0.7) than at 250 or 200 °C (mean critical a_w of 0.51 $P = 0.01$) (Table 3). On the other hand, HMF formation in S-CK was associated to a significantly lower critical a_w (0.51) as compared to G-CK (0.64, $p = 0.01$) and F-CK (0.57, NS). This difference in critical a_w between S-CK and F- or G-CK highlight the different kinetic of HMF formation.

4. Conclusion

This paper describes the complex and interrelated evolution of physical and chemical parameters in a cookie model during baking. The increase in temperature in the core of the cookie conditions the degradation of the sugar. In the same time, water evaporates and water activity decreases to a critical value (0.5–0.7) allowing the formation of HMF from reducing hexose. In turn, HMF is a key product in the development of browning in cereals. We observe that below an oven temperature of 300 °C associated to temperature in the core of the cookie of 105 ± 6 °C, S-CK produce less HMF than G- and F-CK. This is explained by the relative stability of sucrose at such temperatures and the need for a lower water activity as hexose to form HMF. Inversely, at an oven temperature of 300 °C associated to a temperature in the core of the cookie of 120 °C, sucrose is totally hydrolysed, and fructose and glu-

cose released seem more reactive than pre-existing hexose in G- and F-CK in producing HMF. Moreover, at this high temperature HMF is formed since a_w as high as 0.7. Consequently, if we compare at the reference browning and baking time the HMF concentration in cookies processed at different temperatures and with different formulations, the lowest HMF concentration is observed for S-CK at 200 °C (8.34 ± 0.74 mg kg^{-1}) and the highest for S-CK at 300 °C (585.94 ± 28.82 mg kg^{-1}). On the other hand, whatever the temperature, fructose-formulated cookies produce more HMF than glucose. Commercial cookies are generally baked with sucrose at low temperatures (below 250 °C), with a mean HMF of 25.97 ± 14.90 mg kg^{-1} which is in agreement with our observations.

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