Effects of Formulation and Baking Conditions on Neo-formed Contaminants in Model Cookies

M. COUREL[1], L. AIT-AMEUR[2], E. CAPUANO[3], V. FOGLIANO[3], F. J. MORALES[4], F. COURTOIS[1] and I. BIRLOUEZ-ARAGON[2]

[1]UMR 1145 Ingénierie Procédés Aliments, AgroParisTech, INRA, F-91300 Massy, France; [2]AgroParisTech, F-75231 Paris Cedex 05, France; [3]Universita Degli Studi di Napoli Federico II, I-80055 Portici, Italy; [4]Consejo Superior de Investigaciones Científicas, E-28040 Madrid, Spain

**E-mail: mathilde.courel@agroparistech.fr*

Abstract: This work aimed at studying the influence of baking temperature and formulation on the formation of undesirable Maillard compounds called neoformed contaminants (NFC) in a model cookie system. Four NFCs were observed as furosine (FUR), carboxymethyllysine (CML), hydroxymethylfurfural (HMF) and acrylamide (ACR) for three baking temperatures – 150, 200 and 230°C – and three recipe variables as sugar type, fat saturation level and leavening agent. The results showed significant accumulation of all neoformed contaminants along baking with specifically strong temperature dependence for HMF and ACR while CML and FUR were more time dependent. The type of sugar used is determinant regarding NFC formation: glucose tends to generate more HMF than sucrose at low baking temperatures and more CML whatever the baking temperature. The substitution of sugar by a sugar alcohol like maltitol, allows strongly limiting HMF production. Surprisingly, no promoting effect of ammonium carbonate on ACR could be evidenced.

Keywords: cereal products; Maillard reactions; baking temperature; newly formed compounds; sugar type

INTRODUCTION

Heat treatment of foods is a key operation in the industry resulting in the development of a large range of flavours and tastes through the Maillard reaction. However, some of the Maillard products called Neo-Formed Contaminants (NFC) are currently suspected to have deleterious health effects. The objective of this work was to analyse the influence of the ingredients and of the heat treatment, on NFC formation in cookie types of products. Four NFC were selected for this study. FUR is a marker of early Maillard reaction; CML, HMF and ACR are relatively stable advanced Maillard products with possible negative health impact, which presence has been related to formulation and processing conditions in cereal products (Ait-Ameur *et al.* 2007; Claus *et al.* 2008). To study the thermal effect on NFC formation, kinetic data were generated under three baking temperatures (150, 200 and 230°C). Three recipe variables were observed: sugar type, fat saturation level of a single palm fat and presence or absence of ammonium carbonate as leavening agent. The chemical responses (FUR, CML, HMF and ACR) were partially recorded due to the high number of chemical analyses required.

MATERIAL AND METHODS

Model cookies were prepared from wheat flour (60.78%), sugar (11.92%) – sucrose, glucose or maltitol – high or low hydrogenated palm fat (9.54%), water (17.27%), ammonium hydrogencarbonate (0% or 0.33%) and salt (0.16%). The dry ingredients were mixed for 2 min at room temperature (mixer Hobart N50, Troy, OH, USA). The water and the melted fat (45°C) were then incorporated to the powder mix. The dough was allowed to rest for 30 min at 25°C. It was then rolled mechanically and cut into disks of 5 mm thickness and 7.5 cm diameter. Batches of 5 cookies were baked in the centre of a domestic oven (SPAG-ENSIA, Massy, France) set at 150, 200 or 230°C for a final time of 32, 18 and 15 min, respectively, to obtain a final comparable water content of 5%. The kinetic data were generated from independent baking operations made in duplicate for intermediate times and in quadruplicate for final baking time. After baking, the 5 cookies were allowed to cool down for 10 min; they were ground together into powder with a domestic mixer and stored at –18°C before analysis.

The measuring method of ***FUR*** and ***CML*** was adapted from Charissou *et al.* (2007), comprising sample preparation by defatting and protein extraction before hydrolysis with 6M HCl. CML was quantified by selected ion monitoring on a FOCUS GC (Thermo Electron Corporation) gas chromatograph and FUR by MS-MS detection.

HMF was measured according to the method reported by Capuano *et al.* (2008). After water extraction and protein precipitation, HMF determination was done by an HPLC system composed of LC-10AD class VP pumps, LC18 column (SUPELCOSIL) connected to a UV/VS detector (SPD 10 AV VP, SHIMADZU, Japan) set at 280 nm.

ACR measurements were performed according to Senyuva and Gökmen (2006), by LC-MS (AGILENT LC-1100, AGILENT Quadrupole MS detector) equipped with a ODS column (25 × 0.46, 5 µm).

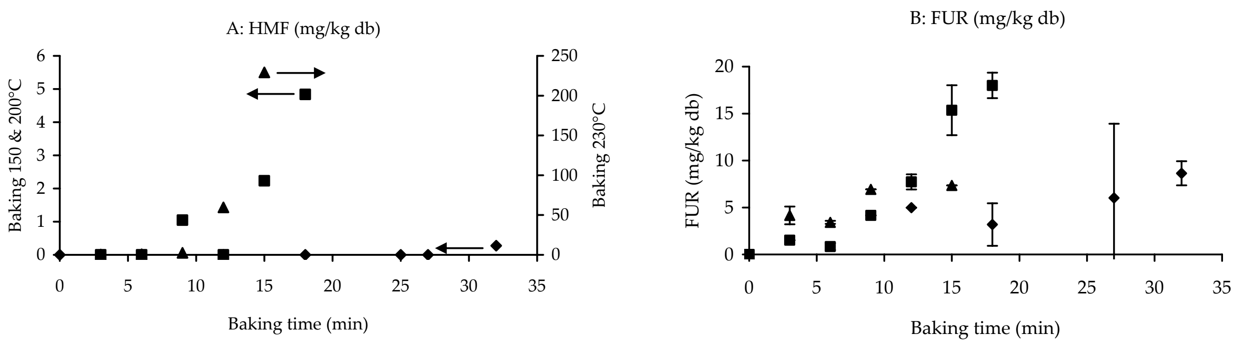
RESULTS AND DISCUSSION

Examples of the accumulation kinetics of HMF, FUR, CML and ACR during baking are given in Figure 1 for a formula containing sucrose and highly saturated palm fat. The concentration of all neoformed contaminants increased during baking all the more that the baking temperature was high (Table 1). The thermal dependence is particularly pronounced for HMF and ACR: for a comparable final water content of 4.3% db (dry basis), HMF concentrations of 0.3, 5 and 229 mg/kg db are obtained respectively at baking temperatures of 150, 200 and 230°C; ACR is absent in the model cookies baked at 150°C and is doubled between 200 and 230°C. CML and FUR appear to be more time rather than temperature dependent.

Glucose induces significantly higher HMF accumulation versus sucrose at 150°C while this trend is reversed at 230°C. Significantly higher levels

Table 1. Concentration of neoformed contaminants as function of baking temperature and type of sugar used in the formulation of model cookies. Standard deviation (SD) corresponds to whole process variability for HMF and ACR and to analytical variability for CML

Baking temperature (°C)	Glucose	Sucrose	Maltitol	Sucrose/no leavening agent
HMF ± SD (mg/kg dry basis)				
150	4.0 ± 0.5	0.3 ± 0.2	0	/
200	18 ± 11	5 ± 4	1.4 ± 0.4	/
230	41 ± 18	229 ± 126	2.8 ± 1.3	122 ± 48
CML ± SD (mg/kg dry basis)				
150	25.8 ± 0.1	8.8 ± 2.5	5.7 ± 1.3	/
200	22 ± 4	11.9 ± 1	10.9 ± 1.8	/
230	25 ± 2	10.3 ± 1	16.4 ± 0.6	27.6 ± 0.4
ACR ± SD (µg/kg dry basis)				
150	/	0.00	/	/
200	/	60 ± 2	/	/
230	/	124 ± 39	/	115 ± 15



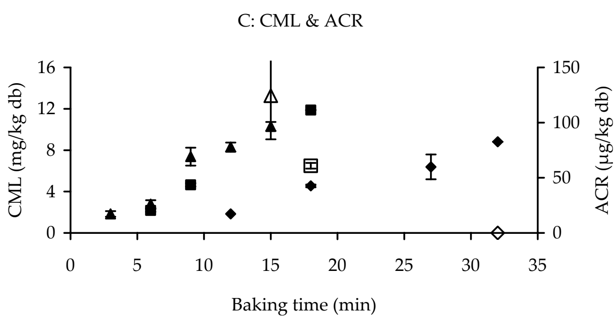


Figure 1. Accumulation of NFC in a model cookie (sucrose), baked at 150°C (◆), 200°C (■) and 230°C (▲). A: HMF B: FUR and C: CML, ACR (empty signs). The standard deviations correspond to whole process (HMF, ACR) or analytical (FUR, CML) variability

– from 2 to 5 fold increase – of CML are found in glucose formulas for all baking temperatures. As was reported by Ait-Ameur *et al.* (2007), the sucrose hydrolysis producing simple reducing sugars seems to be the limiting reaction at low temperatures whereas it is favored at high baking temperatures. Substituting the sugar by a sugar alcohol like maltitol allows reducing by 15 fold the level of HMF but does not seem to affect CML. The impact of the type of fat did not appear to be significant (data not shown) probably because the two hydrogenated palm fats selected in these experiments were too similar regarding saturation level. A comparison of the saturated palm fat to an unsaturated fat would be more relevant to study possible interactions between Maillard reaction and lipid oxidation. Finally, HMF appeared to be affected by the presence of ammonium carbonate whereas no promoting effect was observed on ACR, contrary to what was found by Amrein *et al.* (2006). This observation might be partly due to the limited number of ACR analysis being insufficient for discrimination purposes.

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