

Hydroxymethylfurfural: An Indicative Parameter of Heat Damage in Cereal Products

L. AIT AMEUR^{1*}, M. ZUDE¹, G. TRYSTRAM² and I. BIRLOUEZ-ARAGON¹

¹INAPG, Laboratoire de chimie analytique, Paris, France, *E-mail: aitameur@inapg.fr;

²ENSIA, UMR GenIAL, Massy cedex, France

Abstract: The main chemical changes occurring during biscuit cooking result from two complex reactions involving reducing sugars: the Maillard reaction and caramelisation, both of them being responsible for non enzymatic browning. These reactions were assessed by determinations of furosine (Fu), hydroxymethylfurfural (HMF), and colour at different times (each 2 min) of the cooking process (10 min). The surface colour of biscuits was carried out with $L^* a^* b^*$ parameters, and the global browning development was measured by the reflectance of the whole biscuit in powder. Simultaneous formation of HMF, Fu and browning were investigated to evaluate the correlation between parameters during cooking and identify the best indicators of the biscuit quality. Fu was almost stable during the first 4 min before decreasing in the last 6 min. In contrast, HMF exponentially increased after 4 min, when the water activity reached 0.6. Reflectance was linearly correlated to cooking time and was well correlated to HMF. We conclude that HMF could be a useful indicator for controlling the cooking process of biscuits.

Keywords: Maillard reaction; biscuits; HMF; furosine; browning

INTRODUCTION

Biscuits are prepared with wheat flour, sugars, fats and water and cooked at high temperature (> 200°C) for several minutes. The severe heat treatment applied under low moisture conditions strongly favours chemical reactions involving carbohydrates. During cooking, starch and non-reducing sugars such as sucrose are hydrolysed into reducing sugars that can further participate in the Maillard reaction and caramelisation [1, 2].

Fructosyllysine (FL) is considered as the main form of lysine unavailability during the early stage of Maillard reaction in foods, so that it is commonly proposed as an indicator of the nutritional damage during cooking [2–4]. This nutritional control is particularly important in cereal products, where lysine is the main limiting amino acid. FL content is generally evaluated by 2-furoylmethyl-lysine (furosine) generated from its acid hydrolysis [2].

The intermediate stage of the Maillard reaction can be followed by HMF accumulation, a product of hexose degradation, which can also be formed by dehydration of FL [1, 2]. HMF is reported to be

slightly mutagenic, but its toxicological relevance has not yet been clarified [5, 6]. Furfurals, especially HMF, are considered as good indicators of temperature fluctuation during the heat process (sterilisation, cooking) and during storage [2, 7]. Consequently, HMF is often used for process control in pasta drying [3], baking [2, 4, 8] and in baby and breakfast cereals [5, 9, 10].

Simultaneous analysis of HMF and furosine has been proposed to add supplemental information on the cooking process [2, 11, 10].

EXPERIMENTAL

Sample preparation. Biscuits (BI) were prepared from wheat flour (60%), sucrose syrup (30%) and palm fat (10%). After mixing the products for 4 min in a bowl (Hobart, USA), the dough was allowed to rest for 30 min in the oven at 25°C, and was rolled mechanically to reduce the diameter to 3 mm. The biscuits were cooked in an oven (SPAG – ENSIA, France) set at 250°C in vault and plate.

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

Measurements were carried out after 2, 4, 6, 8, and 10 min to study the kinetic of HMF, furosine and browning. Analyses were performed on the central biscuit of a cooking grid.

Temperature during cooking was measured by sensors placed in the core of the biscuits. They were connected directly to a computer that allowed online monitoring.

Analytical determinations. HMF was analysed by HPLC using a reversed-phase C_{18} (EQUISIL ODS 5 μm , 250 \times 4.6 mm) column (CLUZEAU, France) eluted with methanol/sodium acetate 0.04M (10/90) adjusted at pH 3.6 with acetic acid. The flow rate was 1 ml/min. HMF was detected at 284 nm and quantified by external HMF standard (Fluka, Switzerland). Results are the mean values of duplicate analysis expressed as mg/kg BI.

Furosine was analysed by HPLC after sample hydrolysis in HCl 7.8 N for 18 h, using a reversed-phase C_{18} (HYPERASIL BDS 5 μm , 250 \times 4.6 mm) column (SHANDON, France), eluted with 5.6 μM *o*-phosphoric acid and was detected at 280 nm. The amino-acid content of the hydrolysate was measured by the fluorescamine method [12]. A furosine standard (Neosystem, France) was used for calibration. Results are the mean values of duplicate analysis expressed as mg per 100 g of proteins.

Browning was evaluated at the surface of the biscuit by the $L^*a^*b^*$ colour system using a chromometer (Minolta, Japan). The colorimetric parameters L^* , a^* and b^* were referred to a white standard (D_{65} , Minolta, Japan). Browning was evaluated on the biscuit powder by the maximal reflectance intensity measured at 468 nm on a spectrometer (SAFAS, Monaco).

Results are given for three independent cooking processes.

RESULTS AND DISCUSSION

Evolution of the different parameters during the cooking process

Figure 1 shows that the temperature in the core of biscuit follows three periods: in the first period the temperature increased rapidly during about 2 min; while during the second period, it remained stable because of the equilibrium between heat transfer to the biscuit and water evaporation at the surface. In the third period, temperature increased again

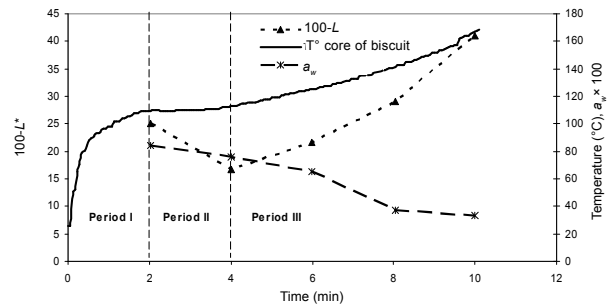


Figure 1. Evolution of temperature, water

until reaching 160°C at 10 min. At the same time, the water activity diminished from 0.80 after 2 min cooking to 0.30 after 10 min. Browning developed at the surface of the biscuit after 4 min.

The kinetics accumulation of HMF and furosine are presented in Figures 2 and 3, respectively.

HMF accumulation followed a first order kinetic (Figure 2). HMF concentration reached 452 mg/kg BI after 10 min. In contrast Figure 3 shows that furosine concentration was almost stable during the first and the second steps of cooking (mean level of 515 mg/100 g), before a slightly decreasing after 6 min. These results confirm previous data reported by GUERRA-HERNANDEZ *et al.* [5].

Figures 4 and 5 show that global browning of biscuit measured by the maximum of reflectance had a better negative correlation with time of cooking ($R^2 = 0.88$) than the L^* parameter, which measured the browning in the surface of the biscuit ($R^2 = 0.72$).

HMF was exponentially correlated to the reflectance ($R^2 = 0.82$) (Figure 6). It was intensively formed from glucose and fructose generated from sucrose hydrolysis at the same time when the browning appears at the surface of biscuit.

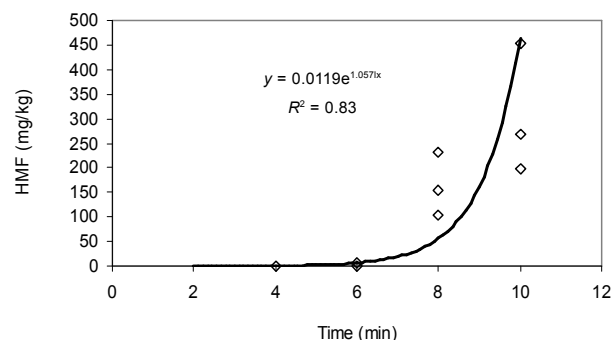


Figure 2. Kinetic accumulation of HMF activity and browning in the core of biscuit

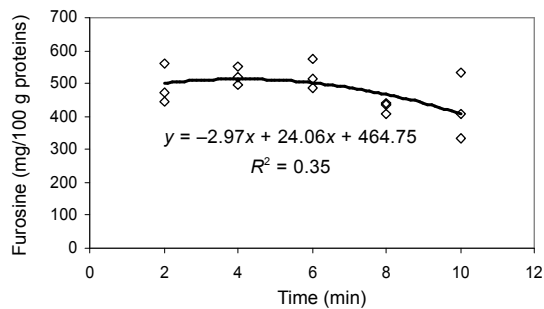


Figure 3. Kinetic accumulation of furosine

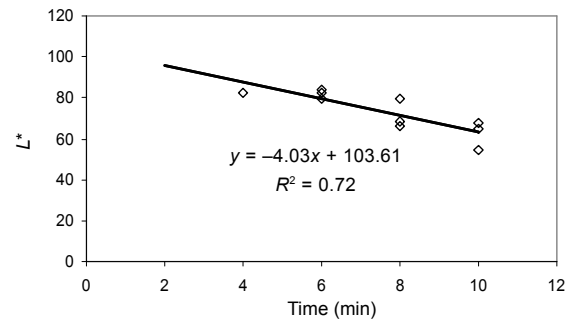


Figure 4. Evolution of 100-L during cooking

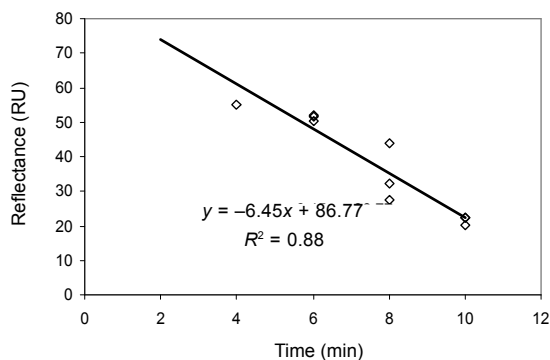


Figure 5. Evolution of reflectance

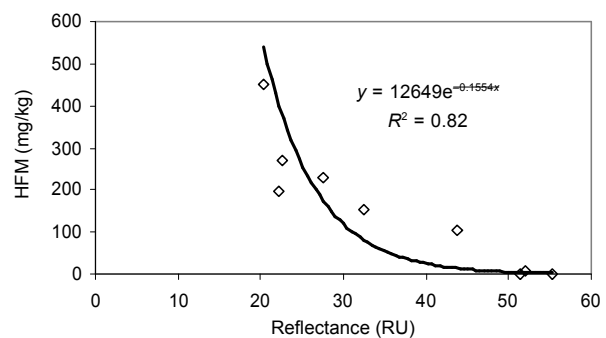


Figure 6. Correlation of HMF with reflectance during heating

CONCLUSIONS

This study shows that measurement of reflectance (468 nm), carried out on the powdered biscuit is a more sensitive physical indicator of the cooking process than colour measurement (L^*) at the surface of the biscuit.

HMF concentration varies exponentially with the cooking time; it appears very sensitive to the temperature of cooking and to the decrease of water activity in the biscuit.

Furthermore HMF appears much more correlated to the browning and the cooking process than furosine, which is degraded at such high temperatures. Thus, HMF can be used to control the cooking process.

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