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# Influence of inulin on bread: Kinetics and physico-chemical indicators of the formation of volatile compounds during baking

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# ABSTRACT

The influence of inulin on the formation and release of white bread volatiles was studied during baking, using an innovative on-line baking extraction device. Kinetic studies were performed to follow the development of crust physical properties and the formation of volatiles responsible for the flavour of breads having different amounts of inulin. It was demonstrated that inulin accelerated the formation of the bread crust and the Maillard reaction. It led to breads with an overall quality similar to that of nonenriched breads, but baked for a shorter time. Correlations between some crust properties and the amount of Maillard volatiles were determined. They showed that crust water activity, moisture and clearness could be good indicators of the Maillard reaction during the baking of bread.

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# 1. Introduction

Being a source of proteins, dietary fibre, vitamins, micronutrients and antioxidants, bread is considered to be of global importance in nutrition ([Dewettinck et al., 2008\)](#page-9-0). Contrary to whole bread, which is relatively high in fibre content (7–8% of dry matter), white bread contains only 2–3% fibre on a dry matter basis ([I.N.B.P., 1999](#page-9-0)). Fibres, and more particularly the soluble ones, like inulin and oligofructose, might help to prevent diseases like intestinal infections, colorectal cancers, obesity, cardiovascular diseases and type II diabetes [\(Franck, 2008](#page-9-0)). Therefore, to improve the nutritional quality of white bread, new formulae enriched in fibres like inulin can be developed.

The rheological properties of inulin-enriched white bread dough and the physical quality of the resulting breads have already been studied by [Collar, Santos, and Rosell \(2007\), Mandala, Polaki,](#page-9-0) [and Yanniotis \(2009\), O'Brien, Mueller, Scannell, and Arendt](#page-9-0) [\(2003\), Peressini and Sensidoni \(2009\)](#page-9-0) and [Wang, Rosell, and Ben](#page-10-0)[edito de Barber \(2002\)](#page-10-0). [Wang et al. \(2002\)](#page-10-0) also compared hedonic scores given to non-enriched and inulin-enriched white breads for grain, crumb smoothness, aroma, flavour and overall acceptability. They showed that inulin-enriched bread had lower scores than non-enriched bread for all these properties. This study thus revealed that inulin could have an effect on the perception of white bread flavour. Yet no work was carried out to understand how it influenced bread flavour properties and aromatic profile.

and especially the fructooligosaccharides produced by its partial hydrolysis, may be involved in the Maillard reaction because of their reducing activities. In both studies, the effect of inulin was studied in aqueous solutions. It could thus be considered whether inulin would have the same effect in a complex matrix, like bread. This hypothesis is worth investigating as Maillard volatiles play a major role in the appreciation of bread flavour quality. Formed during thermal food processing, Maillard volatiles are interesting due to their typical flavour and their high odorant potency ([Schi](#page-10-0)[eberle & Hofmann, 2002](#page-10-0)). Due to their roasty smell, these compounds are generally responsible for the aroma of wheat bread crust, which is appreciated by consumers [\(Grosch & Schieberle,](#page-9-0) [1997\)](#page-9-0). To study volatiles released during the baking of a model cake, [Rega, Guerard, Delarue, Maire, and Giampaoli \(2009\)](#page-10-0) have developed an on-line dynamic HS-SPME (headspace-solid phase microextraction) extraction device in which an SPME (solid phase microextraction) fibre is placed in the oven gas flow. With this device, they extracted volatile compounds released from cake at different baking intervals. They had to perform several baking procedures to obtain the kinetics of volatile release. The present study aimed to understand if inulin influences the

[de Gennaro, Birch, Parke, and Stancher \(2000\),](#page-9-0) and [Huebner,](#page-9-0) [Wehling, Parkhurst, and Hutkins \(2008\)](#page-9-0) demonstrated that inulin,

formation of French-style white bread volatiles, focusing on those coming from the Maillard reaction. For this purpose, an innovative on-line baking extraction device was developed to study the kinetics of bread baking. It was designed so that several SPME fibres could be used simultaneously, enabling the extraction of volatiles released during different time intervals of the same baking. Kinetic





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studies were performed to follow the formation of the volatile compounds responsible for the flavour of white breads (one bread without inulin and two breads with different amounts of inulin). The physico-chemical properties of breads were also followed throughout their baking. Then, these results were used to determine parameters that could be used as indicators of the formation of Maillard volatiles during the baking of bread.

# 2. Materials and methods

# 2.1. Dough-making

Three different white bread formulations were prepared: one without inulin (basic formula), another with 3% inulin (weight/ flour weight) and the last with 5% inulin (weight/flour weight). Inulin formulae (0% and 5%) were both performed twice: the first one was dedicated to the on-line baking extraction experiments; the second one was used to evaluate bread physical qualities throughout the baking. We checked the repeatability of physical measurements and on-line extraction of volatiles on the formula containing 3% inulin. It was therefore performed six times (three for physical measurements and three for volatiles extraction). The basic dough formula contained, on a flour basis: 5% fresh yeast (Michard SAS, Theix, France), 2% salt (Esco France S.A., Levallois-Perret, France), 1% improver (dry flour, Multec datem HP20, aamylase and xylanase, ascorbic acid) (Puratos, Groot-Bijgaarden, Belgium), and 58% water. Type 55 wheat flour was purchased from Moulins Soufflet Pantin (Pornic, France) and inulin was provided by Puratos (Groot-Bijgaarden, Belgium). When 3% or 5% inulin was added, the same amount of flour was removed in order not to modify the dry matter of the dough. Ingredients were mixed in an SP10 spiral mixer (VMI, Montaigu, France) for 1 min and 20 s at 100 rpm and 4 min and 20 s at 200 rpm. The mixed dough  $(2100 g)$  was rested  $(15 min)$  and moulded into two balls. They were rested again (10 min) then rolled out with a rolling pin to obtain thick round homogenous sheets. These were then divided into balls about 48 g by a dividing-moulding machine in order to obtain 44 individual loafs of bread (Bongard, Holtzheim, France). The 44 dough loafs were then placed in a proofing cabinet (Panimatic, Souppes sur Loing, France) for 60 min at 35  $°C$ , 95% relative humidity.

# 2.2. Bread baking

At the end of proofing, the 44 dough samples were baked in a static sole oven (MIWE Condo, Arnstein, Germany) which had previously been designed to study baking kinetics under controlled temperature, humidity, and air velocity conditions. Bread core and crust temperatures were recorded at each kinetic point with K-type thermocouples connected to digital thermometers (AOIP, Ris Orangis, France). Baking was carried out at 230 °C with 0.201 of steam at the beginning of baking. We decided to start the kinetic study when the bread core temperature reached 100 $\degree$ C, which indicated that the dough had acquired a crumb structure [\(Therd](#page-10-0)[thai, Zhou, & Adamczak, 2002; Zanoni, Peri, & Pierucci, 1993\)](#page-10-0). Thus, the kinetic study started at 8 min, and four kinetic points were chosen between this starting point and the end of baking: 11, 14, 17 and 20 min of baking.

# 2.3. Extraction and analysis of volatiles released during bread baking

# 2.3.1. On-line baking and extraction device ([Fig. 1](#page-5-0))

Baking vapours were continuously carried from the oven through a tube 4 m long and 6 mm in diameter. In its central part, vapours were maintained at 80 °C. A humidity sensor (Vaisala, Helsinki, Finland) was placed 3 m along the tube. At the end of this tube, vapours passed through the extraction device. A peristaltic pump (Materiel Physico Chimique Flam Et Cie, Neuilly Sur Marne, France) was placed at the end of the extraction device to draw the vapours at a constant flow rate of 8  $l$  min<sup> $-1$ </sup>. The extraction device was specifically developed for on-line extraction of volatiles. It consisted of a glass tube (25 mm in diameter,  $T = 49 \pm 4.5$  °C), with four openings placed in series every 1.5 cm along its length. Each opening was sealed with a silicone septum. After 8 min of baking (starting kinetic point), four  $75 \mu m$  carboxen/polydimethylsiloxane SPME fibres (Supelco, Bellefonte, PA) were inserted simultaneously into the four septa. CAR/PDMS fibre was chosen because it shows good representativeness ([Poinot et al., 2007](#page-10-0)). Volatiles contained in the baking vapours were thus sampled on the SPME fibres. At each kinetic point (11, 14, 17 and 20 min), one SPME fibre was removed.

# 2.3.2. Evaluation of the on-line baking extraction device performance For the evaluation of the performance of the extraction device,

white breads without inulin were specifically made and baked.

The reproducibility of the extraction using the same fibre placed in the oven gas flow was first verified for three different baking processes (encoded experiment A1). It was compared with the reproducibility of the extraction using four SPME fibres placed simultaneously and in the gas flow, during the same baking process (encoded experiment A2). In all these experiments, SPME fibres (one alone or four simultaneously) were placed in the extraction device at 8 min of baking and were removed at the end of the baking (20 min). For each experiment, mean, standard deviation and percent coefficient of variation (CV% = (standard deviation/mean quantity)  $\times$  100) were calculated, selecting 25 volatiles [\(Table 1](#page-2-0)).

The following experiments (encoded experiment B) aimed to verify that:

- No volatile was present in the oven atmosphere when breads were removed.
- Volatiles were not detached from the SPME fibres and brought by the gas flow during the extraction.

To verify these two points, the four SPME fibres were placed simultaneously in the extraction device at 8 min of bread baking. SPME fibres were all removed at 11 min. Breads were taken out of the oven at the same time and the oven was left open for a few seconds. It was then closed and, after the temperature reached equilibrium, three of the four SPME fibres were replaced in the online extraction device for 3, 6 and 9 min. These SPME fibres were then left in the gas flow for the same time as during the kinetic study (14, 17 and 20 min). The quantity of 20 volatiles which were trapped on the four SPME fibres were compared [\(Table 1\)](#page-2-0).

#### 2.3.3. Chromatographic analyses

Alkanes from n-hexane to n-nonadecane, used to calculate volatile compound retention indexes, came from Sigma–Aldrich (Steinheim, Germany). Standards employed for compound identification were purchased from Sigma–Aldrich (Steinheim, Germany), except acetic acid which was supplied by Panreac (Barcelona, Spain).

The analysis of volatile compounds was carried out with a gas chromatograph Agilent 6890N coupled to a quadrupole mass detector Agilent 5973N, and fitted with a flame ionisation detector. Volatile compounds were separated on a DB-WAX polar capillary column 30 m  $\times$  0.32 mm, 0.5 µm film thickness (J&W Scientific, Folsom, USA). Helium was used as the carrier gas with a constant flow rate of  $2 \text{ ml min}^{-1}$ . The injector temperature was set at 260 °C in split 1:1 mode for 2 min. It was then put in splitless mode

#### <span id="page-2-0"></span>Table 1

Evaluation of the on-line extraction device performance. Experiment A: Verification of the reproducibility of the extraction, when the same fibre was placed in the oven gas flow for three different bakings (A1) and when four fibres placed simultaneously in the extraction device for the same baking (A2); Experiment B: ANOVA with a confidence level of 95% to verify the absence of compounds in the oven atmosphere when breads were removed and to assure that volatiles were not detached from fibres and carried away by the gas flow.



ND, not detected; NS, no significant effect;  $\Delta$ , significant decrease (P < 0.05).

until the end of the run time. The oven temperature was held for 2 min at 45 °C, then increased by  $5^{\circ}$ C min<sup>-1</sup> to  $50^{\circ}$ C, by 0.5 °C min<sup>-1</sup> to 51 °C, by 8 °C min<sup>-1</sup> to 170 °C, and then by 18 °C min<sup>-1</sup> to 230 °C, for 8 min. The mass detector was at 250 °C and operated in scan mode, with electronic impact ionisation (ionisation energy 70 eV) and a mass range of 33–300 amu. A scan rate from 2.72 scans  $s^{-1}$  was used to detect the ions formed. Compound identification was based on the comparison of linear retention indexes (LRI), mass spectra (comparison with standard mass spectra databases: Wiley 6 and an internal database), and injection of standards. LRI were calculated according to the formula proposed by [Van Den Dool and Kratz \(1963\).](#page-10-0) Quantification of volatiles was based on peak areas of data from flame ionisation detector.

## 2.4. Evaluation of bread physical properties

At each of the four kinetic points, six breads were removed from the oven so that the following physical properties could be measured: bread density, crumb hardness, crust colouration, water activity and moisture content.

Bread density and crumb hardness measurements were performed as described in [Poinot et al. \(2008\).](#page-10-0) Crust colouration was measured by a Minolta CR300 colorimeter (Carrières-sur-Seine, France) which displayed the  $L^{\dagger}a^{\dagger}b^{\dagger}$  colour parameters. Breads were placed on their base and four measurements were made at four different locations on their crust. All these analyses were performed in four replicates using four breads.

Water activity  $(a_w)$  and moisture content were determined on a crust sample and on a homogenised sample of crushed bread (crust and crumb). Water activity values were measured using an AquaLab 3TE (Decagon Devices, Pullman, United States). Moisture content was determined by drying the sample at  $100^{\circ}$ C for one week. It was calculated by the weight loss as a percentage of the initial weight of the sample. These analyses were conducted in duplicate using the two breads.

# 2.5. Statistical analyses

A principal component analysis (PCA) using Uniwin Plus 5.1 Software (Sigma Plus, Paris, France) was carried out to compare the three bread formulations (0%, 3% and 5% inulin) obtained at all baking kinetic points (11, 14, 17 and 20 min). It was performed on the crust temperatures, the physical properties and on the total area of the volatile compounds grouped by origin.

Volatile compound data were also subjected to analyses of variance (ANOVA) using Statgraphics Plus 5.1 Software (Manugistics, Rockville, MD, USA). MANOVA (multivariate analyses of variance) was carried out on the area of each volatile extracted to show the effect of baking time, inulin, and their interaction, with a confidence level of 95%. Least significant differences (LSD) multiple comparison tests were then performed with a 95% confidence level.

# 3. Results and discussion

# 3.1. Evaluation of the on-line baking extraction device performance

Table 1 lists the coefficients of variation (CV%) obtained for the 25 compounds (peak areas) by performing the experiments which aimed at evaluating the variability of the baking procedure (exper-

#### <span id="page-3-0"></span>Table 2Areas of volatiles in baking gas extracts; ANOVAs with <sup>a</sup> confidence level of 95%. Compounds are listed according to their origin found in the literature.





Areas of volatiles are expressed in  $\times 10^6$ ; volatiles were identified by LRI (linear retention index on DB-WAX column), by standard mass spectra databases (Wiley 6 and an internal database), and by standard injection. compounds written in italic were not taken into account in the sum and PCA analyses.

MANOVA to determine the effect of baking time and inulin on volatile area: NS. no significant effect: 7 significant increase (P < 0.05): V. significant decrease (P < 0.05): N7 significant decrease (P < 0.05): N7 significa significant increase from 3% to 5% inulin ( $P < 0.05$ ).

Comparison between each volatile quantity extracted during the experimentations: ANOVA and LSD results on each volatile area at a confidence level of 95%: for each compound (in one row), the areas noted with the same lette (a–i) are not significantly different at <sup>a</sup> confidence level of 95%.

Values written in bold illustrate the effect of inulin on volatiles released.

1: Daigle, Gélinas, [Leblanc,](#page-9-0) and Morin (1999).

- 2: Frasse et al. [\(1992\)](#page-9-0).
- 3: Galey et al. [\(1994\).](#page-9-0)
- 4: Grosch [\(1987\).](#page-9-0)
- 5: Grosch and [Schieberle](#page-9-0) (1997).
- 6: Hansen and [Schieberle](#page-9-0) (2005).
- 7: Ho [\(1996\)](#page-9-0).
- 8: [Hofmann,](#page-9-0) Münch, and Schieberle (2000).
- 9: Hurrell [\(1982\)](#page-9-0).
- 10: Jousse et al. [\(2002\)](#page-9-0).
- 11: [Osorio-Cadavid,](#page-10-0) Chaves-López, Tofalo, Paparella, and Suzzi (2008).
- 12: [Richard-Molard,](#page-10-0) Nago, and Drapon (1979).
- 13: Zhang et al. [\(2009\)](#page-10-0).

<span id="page-5-0"></span>iment A1) and the variability of the fibre extraction during the same baking process (experiment A2).

The variation coefficients of the four SPME fibres placed in series (experiment A2) were found to be mostly similar or lower than those obtained with the three replicates of the single SPME fibre (experiment A1). The variability observed in experiment A1, where different baking procedures were considered, was mainly due to the intrinsic variability of the baking process. Experiment A2 indicates that the four SPME fibres trapped the same amount of compounds, whatever their position in the extraction device. Therefore, this extraction device was as efficient and reproducible as the one with a single fibre.

The second part of [Table 1](#page-2-0) (experiment B) shows that the amount of all trapped volatiles (except ethanol) was the same between the four fibres. Yet, three of the four fibres were replaced in the extraction device after breads had been taken out of the oven. This proves that the compounds trapped on the SPME fibres came from the baked breads only, and not from the oven atmosphere. It also reveals that these compounds were not detached from the SPME fibres and brought by the gas flow during the extraction. Ethanol was the only compound for which the trapped amount decreased with time. Therefore, this compound must have been carried away by the pump flow rate. This could be explained by its lowest molecular weight (46 Da) and boiling point (78  $\degree$ C) compared to the other compounds. Even though it was not significant, 1-propanol and 2-methyl-1-propanol showed a biased behaviour like ethanol. Indeed, these two compounds have also low-molecular weights (60.1 and 74.1 Da, respectively).

Therefore, as a precaution, the areas of these three alcohols were not taken into account in the sum of volatiles grouped by origin and for the further PCA analysis.

### 3.2. Analysis of bread physical and chemical properties

Bread physical properties were not evaluated during the same baking as the one performed for the extraction of volatiles. Indeed, for the physical measurements, breads had to be removed from the oven at each kinetic point. Removing breads during the on-line extraction might have had an impact on the quantities of volatiles released in the oven.

To consider the overall effects of baking time and inulin on bread quality, a PCA was performed on bread physical properties and on the total content of volatiles grouped by origin (sum of peak areas, except ethanol, 1-propanol and 2-methyl-1-propanol, as discussed in the Section [3.1\)](#page-2-0) [\(Table 2:](#page-3-0) compounds issued from fermentation (total of classes  $A + B + E + G$ ), lipid oxidation (total of classes  $B + C + F + G$ ) and Maillard reaction (total of classes  $D + E + F + G$ )). [Fig. 2](#page-6-0)a and b display the biplots obtained for the first three principal dimensions. These axes explained 87.6% of the total information. The first dimension opposed water activity, crust moisture content, and crust clearness  $(L<sup>2</sup>)$  to overall volatile amount, crumb hardness and crust temperature. The second axis was positively correlated with bread density and crumb hardness. Finally, the third one was negatively correlated with the colouration coordinates  $\mathbf{a}^T$  and  $\mathbf{b}^T$ . Bread samples were principally differentiated according to their baking time along the first dimension, while the amount of inulin was more correlated with the second axis. Bread samples were more and more positively correlated with this axis as their amount of inulin increased.

As expected, crust water activity, moisture content and clearness decreased while crumb hardness and crust temperature increased throughout the baking time ([Purlis & Salvadori, 2007,](#page-10-0) [2009a, 2009b](#page-10-0)). This result must be linked to the structuring of the crumb and the beginning of crust formation.

Overall quantities of bread volatiles coming from the fermentation, lipid oxidation and Maillard reaction also increased throughout the baking. This suggests that fermentative compounds were continuously released from the beginning to the end of baking, even after the start of the formation of the crust and Maillard reaction. Since it has already been demonstrated that volatiles trapped on SPME fibres come from the breads only, this indicates that fermentative compounds may pass through the crust even when it is completely formed. However, crust used to be considered as preventing bread dehydration, acting as a barrier to mass transfer towards the oven atmosphere ([Purlis & Salvadori, 2009a; Wählby &](#page-10-0) [Skjöldebrand, 2002\)](#page-10-0). Therefore, in the specific conditions of our study, bread crust might not be sufficiently impermeable to impair gaseous release until the end of baking. The amount of compounds coming from lipid oxidation also increased during baking. This confirms previous studies that reported that the hydroperoxides



Fig. 1. On-line extraction device.

<span id="page-6-0"></span>

Fig. 2. Biplots of baking extracts according to their volatile compositions in the first dimensions. Extract code: baking time-quantity of inulin. (a) Biplot in the first two dimensions. (b) Biplot in the first and third dimensions.

formed during dough mixing are cut by homolytic reactions during bread baking [\(Drapon & Richard-Molard, 1979\)](#page-9-0). These reactions led to different compounds such as aldehydes, ketones, acids and esters. Since Maillard compounds are formed during bread baking ([Schieberle & Hofmann, 2002](#page-10-0)), their overall amount increased with the baking time.

As previously reported ([Wang et al., 2002](#page-10-0)), the more inulin breads contained, the denser they were and the harder the crumb was (second and third axes of PCA, Fig. 2). Inulin also seemed to enhance bread crust colouration, as  $\vec{a}$  and  $\vec{b}$  values tended to increase with the amount of inulin according to the third dimension.

Fig. 2 also reveals that breads with 5% inulin and baked for 17 min had an overall quality close to that of breads baked for 20 min and having 0% or 3% inulin. The same was observed for breads baked for 17 min and having 0% or 3% inulin, and those baked for 14 min and containing 5% or 3% inulin. These results suggest that inulin could accelerate bread baking. Crust formation, crust colouration and flavour compound formation were thus enhanced with inulin. As a result, breads with 5% inulin were burnt at 20 min of baking leading to their extreme positions on the first axis, while breads without inulin were acceptable at this baking time.

# 3.3. Effects of baking time and inulin on bread volatiles grouped by origin

Both the baking time and inulin may have an impact on the total fermentative, lipid oxidative and Maillard compounds of bread. It could be thus wondered if such influences would also be observed for every single volatile compound [\(Table 2](#page-3-0)).

A total of 42 compounds were extracted. The amount of 37 of these compounds increased with baking time. Three volatiles issued from fermentation (ethanol, 1-propanol and 2-methyl-1-propanol) were difficult to interpret because of their detachment from the SPME fibres throughout the on-line extractions (as discussed in the Section [3.1\)](#page-2-0). The quantity of ethyl acetate and 3-methyl-1<span id="page-7-0"></span>butanol was not influenced by the baking time. These volatiles are formed during fermentation, before the baking stage. It could be that they were mostly released before the first kinetic point. Therefore, the trapped quantity did not change during the rest of the baking. On the other hand, the other fermentative compounds belonging to classes  $A + B + E + G$  gradually increased throughout the baking time. It could thus be wondered if the permeability of the crust really decreased at the end of the baking, because this would have induced a lower release of fermentative compounds coming from the crumb. The increase in the release of every compound coming from lipid oxidation and Maillard reaction is explained by their generation on the crust under these heating conditions [\(Drapon & Richard-Molard, 1979; Schieberle & Hof](#page-9-0)[mann, 2002\)](#page-9-0).

Maillard compounds (classes  $D + E + F + G$ ) were continuously released throughout the baking, even though the release decreased a little between 14 and 17 min of baking. Furthermore, the release of compounds resulting from the Maillard reaction only (belonging to class D) was particularly high for bread enriched with 3% and 5% inulin between 17 and 20 min of baking, compared to the kinetic periods before 17 min (the release increased by 117.5% for breads enriched with 3% inulin and by 176.1% for breads enriched with 5% inulin between 17 and 20 min). Therefore, inulin seemed to enhance the Maillard reaction, particularly at the end of baking.

The results in [Table 2](#page-3-0) also reveal that inulin had a significant effect on some of the volatiles. Fermentative (classes  $A + B + E + G$ ) and lipid oxidative (classes  $B + C + F + G$ ) compounds were randomly influenced. The area of some of these compounds decreased



**Fig. 3.** Correlation plots for total Maillard compound area and crust  $a_{\sf w}$ , crust moisture content and crust clearness  $\iota^*$ . Plots were drawn between the area values and the  $a_{\sf w}$ (or moisture or <sup>L</sup>\* ) for all kinetic points (11, 14, 17 and 20 min) and for the three bread formulations (0%, 3% and 5% inulin).

<span id="page-8-0"></span>in the presence of inulin (2-methyl-1-propanol, 3-methyl-1-butanol, 3-ethoxy-1-propanol, butyric acid, hexanoic acid, 1-pentanol and 1-hexanol). This could be linked to the ability of inulin to dilute the bread gluten network and to absorb water that would have been used for gluten hydration ([Stojceska & Ainsworth, 2008](#page-10-0)). This may thus limit the interactions between amylose and  $\alpha$ -amylase (as well as for fatty acids and lipoxygenase). An explanation could be that the quantity of fermentative carbohydrates (and hydroperoxides) decreased, leading to a reduction in fermentative (and lipid oxidative) volatiles.

The amount of 18 out of 23 Maillard compounds increased in the presence of inulin which confirms the hypothesis about the effect of inulin on the enhancement of the Maillard reaction. Some of the Maillard compounds (i.e. 2-methylpyrazine, 2-acetylfuran, 5 methyl-2-furfural, furfuryl alcohol and 2(5H)-furanone) were particularly highly released from bread baked for 20 min and containing 5% inulin, resulting in a significant interaction between the baking time and inulin for these compounds.

Furthermore, the comparison of all extracts ([Table 2,](#page-3-0) values written in bold) reveals that two Maillard compounds (pyrazine and 2,5- and/or 2,6-dimethylpyrazine) never appeared in the vapours of breads without inulin, but they were detected in the vapours of inulin-enriched breads baked for 20 min. 2,3- Pentanedione, 2-methylpyrazine, 3-furaldehyde, 2-acetylfuran, 5 methyl-2-furfural, 2-cyclopentene-1,4-dione, 2-acetylpyrrole, benzyl alcohol, and benzaldehyde were present whether the breads contained inulin or not, but they appeared earlier in the vapours of inulin-enriched breads ([Table 2](#page-3-0), values written in bold). Others were released in similar quantities in inulin-enriched bread extracts baked for a short time, compared to non-enriched bread extracts baked for a longer time (2,3-pentanedione, 1-hydroxy-2 propanone, 2(5H)-furanone, 2-acetylpyrrole, maltol, 2,3-butanedione, furfural and benzyl alcohol) ([Table 2](#page-3-0), values written in bold).

Clearly and as previously shown by PCA, the addition of inulin to white breads accelerated the Maillard reaction. It may be that the fructan chains of inulin were degraded, leading to the formation of new low-molecular weight products (glucose, fructose, sucrose and possibly di-D-fructose di-anhydrides) on the crust surface. These supplementary saccharides may have then participated in the Maillard reaction and caramelisation of the crust during bread baking. This resulted in breads being baked for a shorter time but having the same overall aromatic quality as those non-enriched and baked for a longer time.

#### 3.4. Physical indicators of the Maillard reaction during bread baking

PCA results [\(Fig. 2](#page-6-0)) revealed that total Maillard compounds were negatively correlated with crust  $a_w$ , crust moisture and crust clearness  $L^{\dagger}$  (|correlations between factor| >9). Therefore, we analysed the correlations between these three parameters and the quantity of Maillard volatiles [\(Fig. 3](#page-7-0)). It could be seen that there was a linear correlation between these three factors and the total quantity of Maillard compounds. The corresponding correlation coefficients and linear equations could have been calculated. This was then carried out for every Maillard compound. Linear correlations were found between these three factors and the area of each Maillard volatile. The correlation coefficients and slopes of the straight lines were calculated and reported in Table 3.

These results reveal that each Maillard volatile was highly correlated with one, two or three factors ( $R^2 > 0.8$ ). The linear correlations between bread volatile area and these parameters have never been observed before in such a complex matrix as bread. Therefore, during bread crust formation, the Maillard reaction was influenced by the moisture content of the sample. Since browning results from advanced Maillard reactions [\(Hurrell, 1982](#page-9-0)),  $\hat{L}$  was also correlated with the amount of Maillard volatiles formed.

As illustrated in [Fig. 2](#page-6-0) for total Maillard compounds, the linear equations show at which value (crust  $a_w$ , crust moisture and  $L^{\dagger}$ ) each volatile began to be formed. These y-intercepts are reported in Table 3 for every Maillard volatile. Volatiles coming only from

# Table 3

Correlations between quantities of Maillard volatiles, crust  $a_{\sf w}$  crust moisture content and crust clearness  $\it L^*$  . Plots were drawn between the area values and the aw (or moisture or  $L^*$ ) for all kinetic points (11, 14, 17 and 20 min) and for the three bread formulations (0%, 3% and 5% inulin). Points which corresponded to a nil area were not taken into account when drawing the line.

	Correlation coefficient $R^2$			Slope			$v$ -Intercept		
	Crust $a_w$	Crust moisture	Crust L	Crust $a_w$	Crust moisture	Crust $L$	Crust $a_w$	Crust moisture	Crust $L$
D. Compounds resulting from the Maillard reaction									
2.3-Pentanedione	0.47	0.92	0.91	$-2E-07$	$-6E-06$	$-1E-05$	0.82	10.7	49.8
2-Methylpyrazine	0.83	0.92	0.61	$-7E-08$	$-2E-06$	$-4E-06$	0.84	10.5	51.0
1-Hydroxy-2-propanone	0.81	0.79	0.75	$-4E-08$	$-2E-06$	$-3E-06$	0.89	13.2	56.8
3-Furaldéhyde	0.81	0.73	0.64	$-3E-07$	$-1E-05$	$-2E-05$	0.98	15.8	62.8
2-Acetylfuran	0.85	0.85	0.79	$-3E-07$	$-9E-06$	$-2E-05$	0.91	14.0	59.2
5-Methyl-2-furfural	0.88	0.83	0.76	$-6E - 08$	$-2E-06$	$-5E-06$	0.88	12.7	55.9
2-Cyclopentene-1,4-dione	0.93	0.69	0.49	$-3E-07$	$-8E - 06$	$-2E-05$	0.88	11.4	54.0
Furfuryl alcohol	0.97	0.87	0.80	$-9E - 09$	$-3E-07$	$-7E-07$	0.91	14.0	58.5
2(5H)-Furanone	0.92	0.78	0.71	$-9E - 08$	$-3E-06$	$-7E-06$	0.89	13.2	56.8
Phenol	0.90	0.81	0.79	$-8E - 08$	$-3E-06$	$-6E - 06$	0.97	16.1	63.3
2-Acetylpyrrole	0.54	0.76	0.55	$-2E-07$	$-5E-06$	$-1E-05$	0.86	11.5	54.1
Maltol	0.59	0.78	0.59	$-2E-08$	$-6E-07$	$-1E-06$	0.83	10.7	51.9
E. Compounds resulting from the Maillard reaction and fermentation									
2.3-Butanedione	0.77	0.58	0.46	$-5E-08$	$-2E-06$	$-3E-06$	0.99	16.3	62.6
3-Hydroxy-2-butanone	0.91	0.97	0.89	$-3E-08$	$-1E-06$	$-2E-06$	0.99	17.3	65.5
Acetic acid	0.88	0.93	0.86	$-4E-09$	$-1E-07$	$-3E-07$	0.96	15.9	62.6
Furfural	0.77	0.78	0.77	$-6E - 09$	$-2E-07$	$-5E-07$	0.89	13.4	57.5
Propanoic acid	0.94	0.93	0.87	$-1E-07$	$-4E-06$	$-9E - 06$	0.97	16.1	63.0
3-Methylbutanoic acid	0.83	0.89	0.80	$-6E - 09$	$-2E-07$	$-5E-07$	0.97	16.5	63.7
F. Compounds resulting from the Maillard reaction and lipid oxidation									
Benzyl alcohol	0.75	0.78	0.71	$-4E-07$	$-1E-05$	$-3E-05$	0.92	14.4	59.8
G. Compounds resulting from the Maillard reaction, fermentation and lipid oxidation									
Benzaldehyde	0.85	0.90	0.83	$-5E-08$	$-2E-06$	$-5E-06$	0.94	15.3	62.0

Correlation coefficients written in bold are above 0.8.

<span id="page-9-0"></span>the Maillard reaction (class D) were formed for lower values of crust  $a_w$ , moisture and  $L^*$  than most of the compounds coming from the Maillard reaction and fermentation (except furfural) and from the Maillard reaction and lipid oxidation (classes  $E + G$ and  $F + G$ ). This confirms that these latter compounds appeared at the early stages of baking. Furfural, which comes from the Maillard reaction and fermentation, was formed for crust  $a_w$ , crust moisture and  $\overline{L}^*$  values close to those of compounds coming from the Maillard reaction only. In bread, this compound may thus be mainly formed by the Maillard reaction.

The decrease in crust  $a_w$ , crust moisture and  $\overline{L}^*$  could also be used as an indicator of the progress of the Maillard reaction. [Table](#page-8-0) [3](#page-8-0) reveals that furfural and furan compounds (3-furaldehyde, 2-acetylfuran, furfuryl alcohol, 2(5H)-furanone, 5-methyl-2-furfural but also furfural) first appeared at high values of crust  $a_w$ , crust moisture and  $L^{\dagger}$ . They were followed by carbonyl compounds (phenol, 1-hydroxy-2-propanone and 2-cyclopentene-1,4-dione). Finally, pyrazine derivatives (2-methylpyrazine and maltol) were formed at lower values of these parameters. This sequence of formation of bread Maillard compounds as a function of their chemical group, follows the sequence previously reported by Jousse, Jongen, Agterof, Russell, and Braat (2002) in a study of sugar–amine solutions. The fact that 2-acetylpyrrole appeared at lower values of the three control parameters was quite surprising as it was found to be generated during the first stages of the reaction by Jousse et al. (2002). In addition, 2,3-pentanedione should normally have been formed at higher values of crust  $a_w$  according to the sequence of formation of Maillard compounds (Jousse et al., 2002). The low correlation factors calculated between the quantity of both compounds and the three parameters could explain these findings. As a result, the regression plot was not precise, which distorted the value of the Y-axis original coordinate.

Such results underline that the kinetics of formation of the different Maillard chemical classes tends to be similar in model systems (sugar–amine solutions) and in a complex matrix like bread. As a result, a simple physical characterisation (crust  $a_w$ , crust moisture and crust clearness) of bread crust could be used to further predict and control the formation of Maillard compounds during bread baking. Moreover, we now know at which values of crust  $a_w$ , crust moisture and  $\overline{L}$ , some specific Maillard compounds are formed during bread baking.

# 4. Conclusion

By developing an on-line baking extraction device, it was possible to analyse the impact of inulin on the formation and release of French-style white bread volatiles. It was demonstrated that inulin accelerated bread baking and, more particularly, the Maillard reaction occurring during baking. This led to breads with a similar overall quality to that of non-enriched breads, but baked for a shorter time. Adding inulin to white breads could have several advantages. First, inulin-enriched breads possess an increased nutritional quality, combined with organoleptic properties similar to conventional white bread, which is better accepted by consumers. Inulin enrichment could thus increase the fibre intake of the population. Secondly, adding inulin to breads could have a positive environmental impact, as such breads could be baked for a shorter time to achieve acceptable organoleptic qualities.

Furthermore, the analysis of the effect of inulin enabled us to determine some crust physical indicators (crust  $a_w$ , moisture and clearness) for the start of the Maillard reaction during the baking of white breads.

To better understand how inulin enhances the bread Maillard reaction, it would be interesting to study the amount of inulin which takes part in it and the quantity of monosaccharides formed by inulin hydrolysis during the first stage of this baking process. In addition, it would be useful to investigate the perception of breads enriched or not with inulin and baked for different times and to link it with the variation of the quantity of every compound present in the breads. By comparing sensory results with bread aromatic profiles, the quantity of selected volatiles at which the sensory perception becomes different could be measured. This would also indicate if the physico-chemical properties of the breads shown during this study are perceived by consumers.

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