INTERACTION OF TEMPERATURE/TIME AND HUMIDITY ON THE GENERATION OF WHEAT BREAD FLAVOUR

Maaruf, A.G[1], Linforth, R.S.T[2] & Taylor, A. J.[2]

[1]Program of Food Science, Universiti Kebangsaan Malaysia
43600 Bangi, Selangor, Malaysia
[2]Samworth Flavor Laboratory, Division of Food Sciences, University of Nottingham
Sutton Bonington Campus, Loughborough, LE12 5RD, United Kingdom.

ABSTRACT. *A mini oven with controllable parameters (namely temperature/time, gas and steam flow) was systematically developed to produce mini bread samples (1g weight). The mini oven was used to investigate the effect of processing on crust colour, moisture content and flavour generation. This allowed a study of the chemistry of the Maillard reaction in the breadmaking process as a function of dough composition and processing conditions. These factors are difficult to handle if conventional ovens and normal size of commercial bread (about 0.6-1.0 kg) are used. The amount of volatiles in the samples was assessed via rapid solvent extraction, distillation to separate volatiles from fat and identification and quantification by GC-MS. Volatile compounds extracted from the mini bread consisted primarily of aldehydes, ketones, alcohols, pyrazines, thiazole and pyridines. With a rapid and reproducible assay in place, the generation of volatiles was investigated at different levels of baking processes (namely temperature, time and humidity). Flavour amounts in mini bread increased with the increase of baking temperature and time and oven humidity (steam). The procedure presented in this study is time saving and beneficial as small samples and quantities were used.*

KEYWORDS. Baking; extraction; thermal flavour; wheat bread; GC-MS

INTRODUCTION

Bread, one of the staple foods consumed by mankind is based on flour derived from the cereal wheat (Cauvain and Young, 1998). Wheat bread is a multiphase and multi-component system comprising proteins, polysaccharides, lipids, gas and other minor nutrients. It has a foam structure, with continuously growing gas bubbles dispersed in an apparently homogenous semi-solid aqueous dough phase (Ganz *et al.*, 1999). The quality of bread is influenced by several factors, including composition of flour, dough formulations, and baking processes. The term quality is very broad, in this study the quality is focusing on the generation of flavour from the breadmaking process (namely temperature/time, gas and steam flow). The flavour of fresh bread is due to a combination of the enzymatic and chemical reactions during fermentation of the dough and the thermal changes occurring in the oven, particularly associated with the formation of a brown crust (Baker *et al.*, 1953). The Maillard reaction is chiefly responsible for the development of the attractive bread flavour and typical brown coloration of the bread crust developing (Lindenmeier and Hofmann, 2004).

The control of bread flavour quality requires an understanding of the key chemical reactions involved in the formation of the quality attributes. It is important to understand that the changes during the breadmaking process will affect the flavour, and inconsistencies in flavour may reduce consumer acceptability. This study was to gain knowledge and better understanding of flavour chemistry characteristics in the wheat bread when baked at different breadmaking processes and different dough compositions. The completion of bread baking process in this study was observed by two properties of the product; its colour and its moisture content and this criterion was also used by Wade (1995) in their bread baking study. There are three steps involved in the production of bread: dough formation, fermentation, and baking. Dough develops a gluten network during mixing due to protein interactions. This elastic matrix expands as a result of gas generation during fermentation (Bietz, 1992). The baking process is usually performed by conventional heating, during which heat is transferred by convection from the heating media by radiation from the oven walls to the product surface followed by conduction to the centre (Demirekler *et al*., 2004).

Previous work reported in the literature has involved the baking process under defined conditions (i.e. temperature and time) followed by the extraction and the quantification of the flavour compounds. While this approach is effective and successful in isolating and identifying the volatiles from the bread products baked in the conventional oven (i.e. Jackel, 1969; Mulders *et al*., 1973; Richard-Molard *et al*., 1979; Folkes and Gramshaw, 1981; Schieberle and Grosch, 1991; Grosch and Schieberle, 1997), it is time consuming and requires a large amount of sample and organic solvent. It is therefore of interest to develop a new tool (mini oven) and improve the analytical methods that can mimic conditions aforementioned with easy handling, rapid methods and reproducibility. In this study, the developed mini oven has the potential to bake a smaller size bread (factor of 600 to 1000 smaller) than normal bread baked in conventional oven. The improved analytical methods (extraction and distillation) described in this study were used successfully to isolate and extract the small amounts of expected volatiles in the mini bread samples. The objective of this study was to get an understanding of the interaction of baking temperature/time and the contribution of steam amount (water vapour) in the mini oven to the bread chemistry characteristic.

EXPERIMENTAL PROCEDURES

Mini bread Baking

In order to simplify the investigation as far as possible, only those ingredients absolutely essential to proper baking performance and crust formation were included. Ingredients such as milk solids and butter were deliberately omitted, since they can contribute pronounced flavours of their own. The formulations used are water 350g, salt 10.1g, sugar 22.3g, strong white flour 660g, dried yeast 4.2g (1kg batch bread). Bread dough was prepared using the same formulation as described. Then the dough was mixed (45min) and proved (45min) in a domestic bread maker. About 1.9- 2.0g dough (initial moisture 40.9 ± 0.2%) was placed on a baking tray and immediately put inside the heated sample cell in the oven. Initially, the oven was heated from a start temperature of 30ºC to the oven temperature required (e.g 105, 113, 120 and 140ºC) of 15ºC/min temperature ramp. Then, the final temperature was isothermally held for 30-60 min depending on the baking time required.

Mini oven for mini bread baking

The mini oven system consisted of an oven, a sample cell (c) and a steam producer (b) (Figure 1). Steam was generated by pumping (Modifier pump, Suprex-Anachem, USA) water at 0-800 µl/min, through steel tubing inside the oven (GC Oven-Sigma 3B, Perkin Elmer), then it was passed into a steel capillary tubing which occupied one-quarter of a 2m heated (120ºC) transferline (Hillesheim HT-40, 230V, 16A). Water and N_2 (2l/min) entered the transferline counter current, so the water was effectively vaporised in steam and introduced into the sample cell. The N_2 flow through the transferline was controlled by metering valves and measured by flowmeter (AALBORG, GFM 171) and was maintained at 2 l/min during the baking process. Steam/N_2 mixtures passing through the sample cell were maintained at a controlled flow rate of 5ml/min using a combination of needle and metering valves. The rest of the gases were vented to the atmosphere.

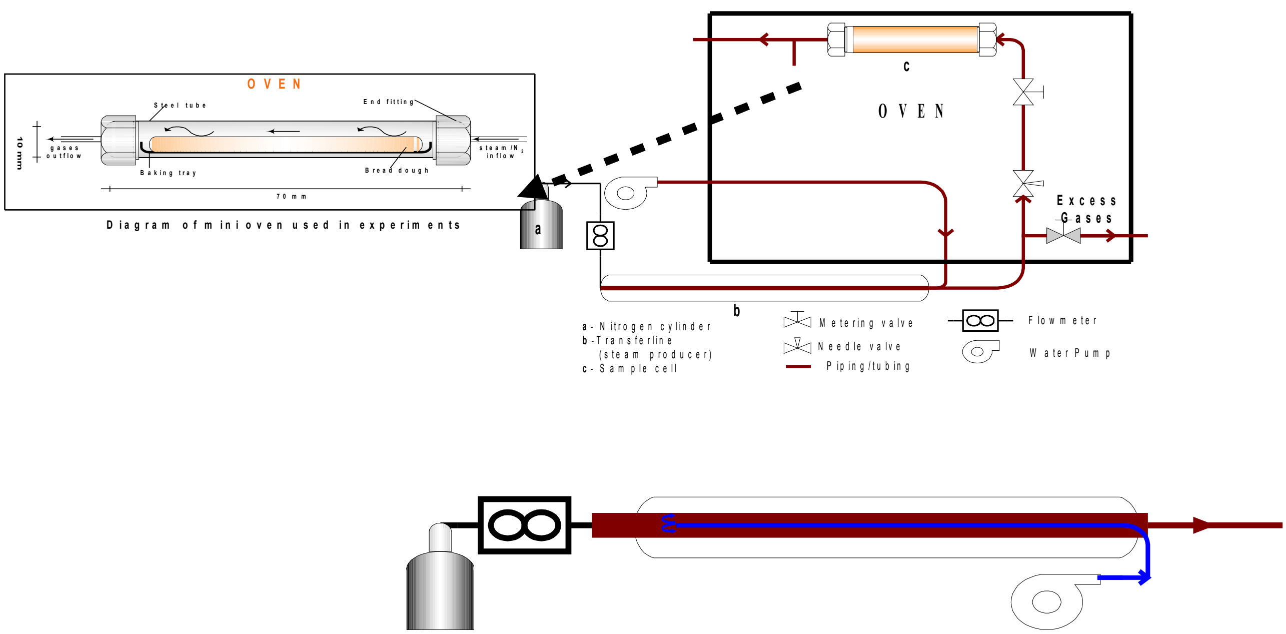

Figure 1. A Schematic Diagram of Mini Oven (Reactor) with Associated Gas and Steam Flows

Isolation and Extractions of volatile

After baking, the mini bread was frozen in liquid N_2, and then ground with a pestle and mortar. About 1g of bread powder was transferred into a test tube fitted with a stopper, 3ml of dichloromethane was added, and then mixed using a Flask Shaker SF1 (Bibby-Stuart Scientific, UK) at 200 oscillations/min for 1 h at room temperature. Dichloromethane was added with 2-pentanone, octanol and 2-isobutyl-3-methoxypyrazine (1ppm each) as internal standards to ensure correct selection of GC peaks and a retention time comparison. A glass pipette was used to remove 1ml of the supernatant for distillation without further concentration.

Vacuum distillation

The distillation apparatus consisted of two round bottom flasks (one heated on a water bath at 90ºC and the other cold on ice/water) with centre and side sockets. These were linked by a glass elbow. The heated flask side arm was fitted with an adapter containing a silicone septum seal. The vacuum in the apparatus was decreased to 27 inHg using a vacuum pump (LABOPORT, KNF-Neuberger) and the valve between the pump and apparatus closed to seal the system. A set volume (1 ml) of extract was injected through the silicone septa into the heated flask at 0.1ml/s over the course of 30 s. Distillation of volatile compounds occurred via evaporation from the heated vessel (maintained at approximately 90ºC) and condensation in the chilled vessel. The distillate was then collected via a glass pipette.

GC-MS and Identification of compounds

A gas chromatograph (GC8000 Series, Fisons Instruments, Loughborough, UK) was connected to an EI Mass Spectrometer (MD800, Fisons Instruments) operated in positive selected ion mode, monitoring ions over a mass range of 40-200 *m/z.* A 30m fused silica column (0.25mm ID) was used with 1.0 micron thick BP5 coating (non-polar) (SGE Europe Ltd, UK). Sample (1µl) was injected through a splitless injection port at 250ºC. The split vent valve remained closed during splitless injection and was opened about 60 sec after injection. The initial temperature of 40ºC was maintained for 4.5 min, then increased to 200 ºC at a rate of 8ºC/min. A solvent delay of 4.5 minutes was programmed to avoid contamination of the MS with the solvent. The transfer line temperature was 230ºC. Chromatograms were integrated using Masslynx computer software. Peak area values were recorded and further processed using Microsoft Excel.

Identification of the compounds were verified by comparison of their retention time with those of authentic samples, measuring Kovat's indices, and relative retention time of the components and authentic samples to internal standard (2-pentanone, octanol and 2-isobutyl-3-methoxypyrazine). Then, compounds were identified using the MS library (NIST) and if the mass spectrum and the retention times of the compounds were well matched, the identification was considered reliable.

Baking bread at different temperature/time and steam level

Mini bread samples were baked with four levels of baking temperatures (105, 113, 120 and 140ºC) and three levels of baking time (30, 45 and 60min), respectively. The transferline temperature was 120ºC and steam supplied to the system was constant at 301g steam/kg nitrogen. For the effect of different levels of steam, 8 different levels of steam (0, 40, 80, 120, 160, 240, 280 and 320 g steam/kg Nitrogen) were passed through the sample cell at a constant rate of 5ml/min. No steam (0 g steam/kg Nitrogen) treatment was run as a control.

RESULTS AND DISCUSSION

Mini oven and steam producer for mini bread baking

Experiments were performed in a mini oven to study the effect of forced convection of hot and moist gases on mini bread characteristics. The use of steam in this system requires a transport system and the steam producer system was connected by a network of pipelines (tubing) to supply the steam to the sample cell (Figure 1). The five baking conditions were defined by oven temperature, baking time, gas humidity (g steam/kg nitrogen), the flow rate of the water pumped (ml/min) and the flow rate of Nitrogen gas (l/min) introduced into the mini oven system. The mini oven temperature and baking time combination was lower than that normally encountered in commercial bakeries. This was attributed to the fact that the mini oven and samples used were considerably smaller and heat transfer from the oven to the samples was quicker and, as a result, allowed a higher degree of water loss. Consequently, it was necessary to decrease baking temperature and time to obtain the correct degree of baking.

Baking temperature/time vs the generation of volatile compounds

Relationships between processing conditions and generated volatiles were studied. Data were analysed by Partial least square regression (PLS) (PLS toolbox version 3.5, Matlab version 7.1). The results of the PLS analysis are presented in Figure 2. The Y axis shows Regression Vector Value plotted against the 17 volatile compounds. High positive Regression Vector Values relate to high baking temperatures and long baking times. Negative values relate to low baking temperatures and short times. The height of the bars shows the correlation between the compound and the temperature x time vector. It is clear from Figure 2 that some compounds increase with a more intense baking process (high temperature /long time) while others decrease as they are more strongly correlated with low intensity baking. Pyrazine compounds increased in concentration with intense baking, however, some aldehyde and most alcohol compounds decreased with the increase of baking temperature x time. The higher baking temperature and the longer baking time had a greater effect on the generation of 2,3,5-trimethylpyrazine and 2-acetylthiazole. The concentration of 2-methylpyrazine, 2-furaldehyde, 2-furanmethanol and heptanal were moderately increased with the increase of this factor.

However, a lesser effect was shown to the generation of ethylpyrazine, 1-octen-3-one and phenylacetaldehyde (Figure 2). Results were in agreement with other investigators (Maga and Sizer, 1978; Fors and Erikkson, 1986; Bredie et al., 1998) who reported that pyrazine formation increased with the higher temperature and lower moisture level. In this study, the baking temperature and time factors did not significantly affect the generation of 2-acetylpyridine. 2-Acetylpyrazine showed a strange behaviour where its concentration decreased with an increase of baking temperature x time.

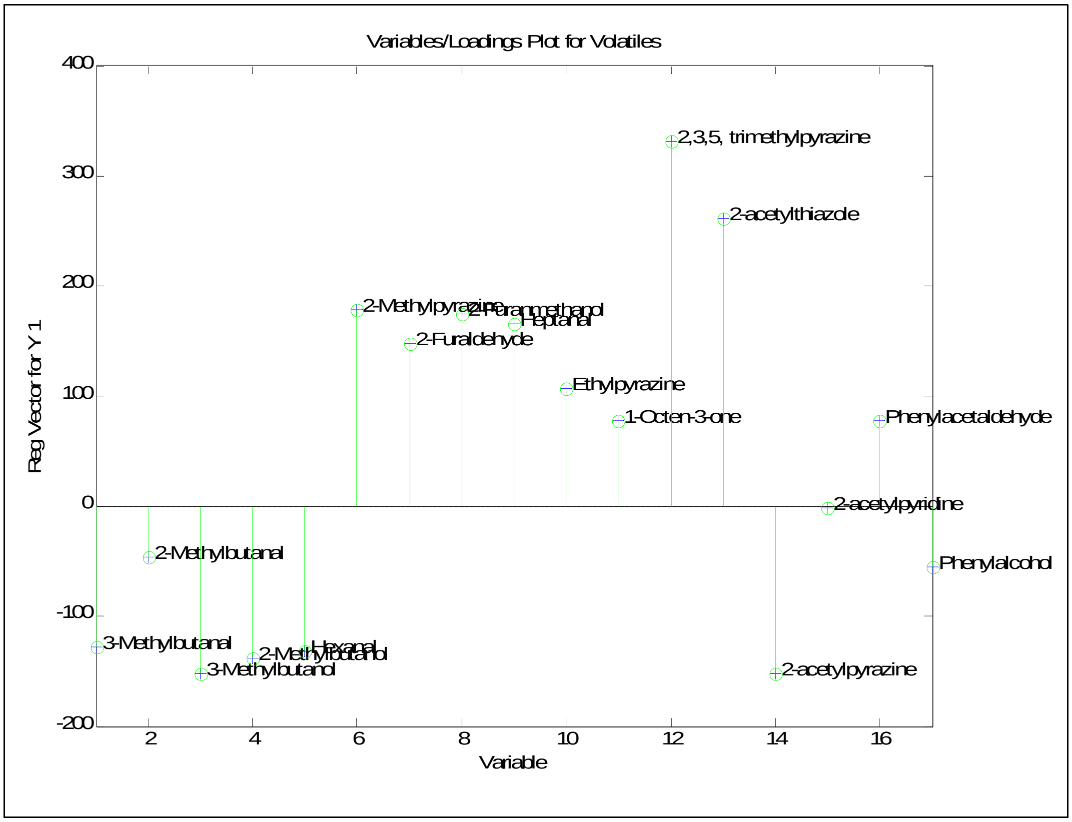

Figure 2. The Interaction of Different Levels of Factors Baking Temperature x Time (Y-axis) to the Generation of the 17 Volatile Compounds (X-axis) in Mini Bread

Comparing volatile generation in mini bread and commercial loaves requires some caution. Since the heat penetration in normal bread dough was slow (Schulerud, 1977), baking the smaller size of mini bread dough (1g) might allow quick heat penetration into the dough resulting in different rates of mass transfer and thermal reactions including browning reaction, gelatinization and enzymatic reaction (Therdthai, 2002). Therefore the variation in the generation of bread flavour compounds in this study and in previous studies was difficult to compare.

Effect of oven humidity (steam) on the flavour generation

This section was investigated the effect of the humidity changes in the baking oven on the generation of volatiles. The humidity levels in the mini oven were altered by introducing steam (0-320 g steam/kg nitrogen) into the gas that flowed over the sample. A standard baking procedure was used (120ºC; 30min; dough moisture contents 40.9%). Figure 3 shows the effect of humidified air on the final water content of the baked bread (top line, solid circle). As humidification increased, the final water content increased from 17 to 23%. There are two possible explanations for the phenomenon, i) high humidity levels reduce the rate of evaporation from the water film on the bread surface into the gas phase (Xue *et al.*, 2004) and ii) there may be uptake of moisture from the gas phase by permeation into the sample (Sommier et al., 2005).

In this latter mechanism, the condensation may also contribute to sample heating as the latent heat of vaporisation is released. Eliasson and Larsson (1993) reported that, a continuous steam flow into the baking oven increased the product surface temperature and increased the heat transfer coefficients (Walker, 1987). In a dry oven, high water diffusivity could bring water to the surface faster and its evaporation would prevent the surface temperature increasing past a certain temperature (Zhang *et al.*, 2005).

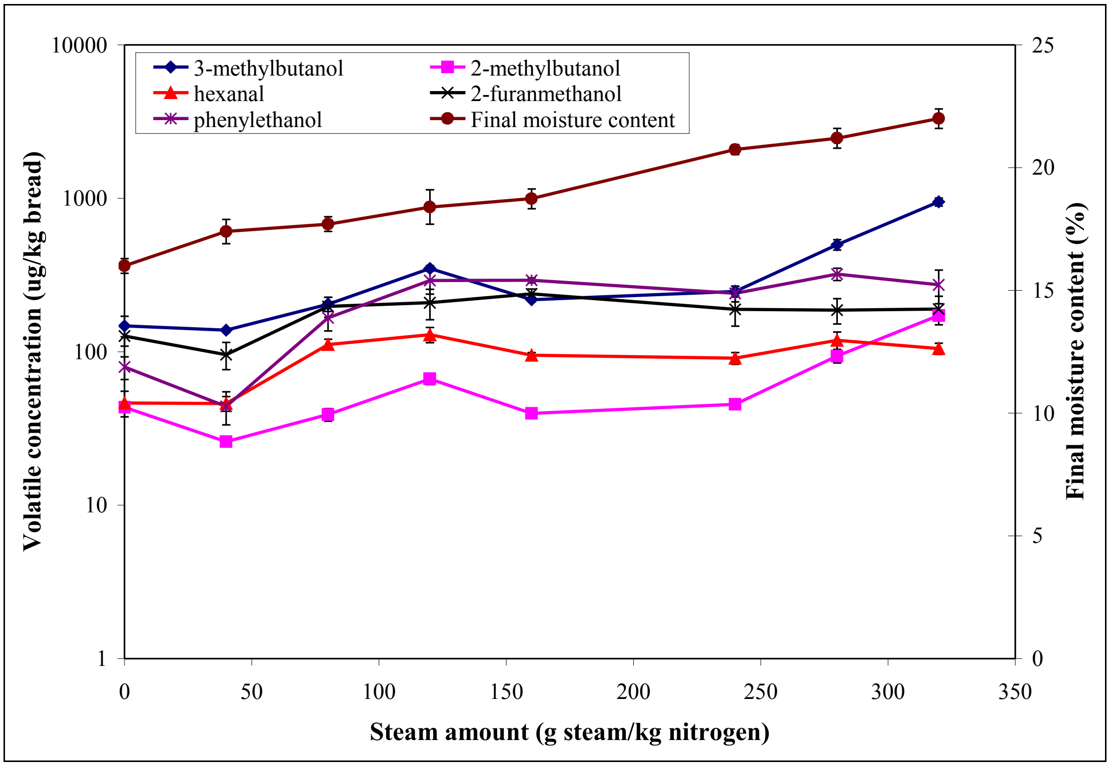

Figure 3. Final Moisture Content and Production Trends of Volatile Compounds in Mini Bread Baking at Different Amount of Steam (g steam/kg nitrogen)

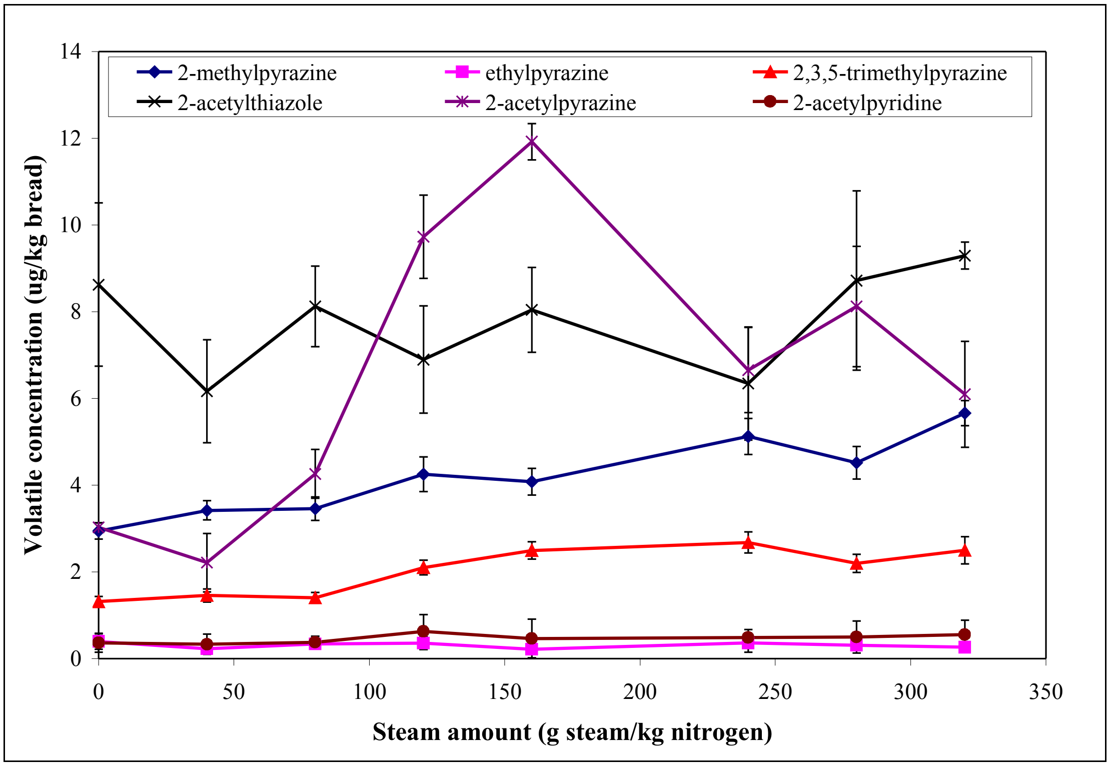

Figure 4. Production Trends of Volatile Compounds in Mini Bread Baking at Different Amount of Steam (g steam/kg nitrogen)

Figure 3 also shows the effect of humidification on the production of some volatile compounds. The volatile compounds show a significant increase with moisture content (factor 3 to 7 times higher). The five compounds are the same group that showed increases in production when dough water content was changed. These compounds seem very sensitive to water content although whether this is due to mobility, concentration through water migration or due to the fact that water is a reactant in their formation is not clear. The latter explanation may apply to the formation of the four alcohols but does not adequately explain formation of the fifth compound, hexanal.

Figure 4 shows the effect of humidification on heterocyclic compounds. For all except 2-acetylthiazole, the level of humidification has little effect although there are some signs of an increasing production with increasing humidification. 2-Acethylthiazole however, exhibits a very different behaviour with a 4 times increase in production as steam content rises from 0 to 150 g/kg nitrogen, followed by a decrease above that value. The anomalous behaviour of 2-acetylthiazole is difficult to explain. The changes are large compared to the error bars associated with the analytical method so the changes do seem to be real rather than random effects.

CONCLUSION

The capability of baking a small sample in mini oven reactor with the complementary rapid extraction and distillation methods developed in this study makes it possible to handle and study the complex procedures (i.e monitoring the changes of volatiles at different level of temperature and time) which involved many baking and extraction steps which are impossible when using a conventional oven and normal size (i.e 1kg) loaf of bread. In this study, the fact that time, temperature and water content are inextricably linked when samples like these are heated. Since these factors affect the Maillard reaction as well, then it is not surprising that a seemingly simple change in water content can have significant effects on Maillard chemistry. Therefore these experiments have to be interpreted within certain limits. They can be related to real world situation and answer commercial questions such as "what effect does steam baking have on flavour generation". However they measure the net effect of many interlinked processes and cannot provide precise information on the mechanisms that cause the changes.

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