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Chemical changes during cooking of wheat

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Chemical changes occurring during the cooking of wheat have been measured in whole grains and in ground wheat. Changes in the gross composition of whole wheat (decreases in the levels of reducing sugars and amino acids) suggested that the Maillard reaction was taking place. Since the water activity of wheat changes during cooking, experiments were performed to study the effect of initial water activity on a number of parameters. Water production, which is symptomatic of early stages in the Maillard reaction, was greatest at $a_{\mathrm{w}} = 0{\cdot}45$. Addition of sulphur dioxide had no effect on these results. Volatile production was greatest at $a_{\mathrm{w}} = 0{\cdot}64$ but comparison of the volatile profiles at different water activities was not possible due to high intra- and inter-sample variation. There was little sign of typical Maillard volatiles in these samples. Colour development decreased with increasing water activity and sulphur dioxide had little effect, suggesting that Maillard and phenolic oxidation play minor roles in colour formation. Although the Maillard reaction seems to occur in heated wheat samples, its role in colour and volatile formation during cooking appears to be minor.

INTRODUCTION

Cooking of wheat is the initial operation in the manufacture of wheat-based breakfast cereal products. During cooking, the grain is hydrated to some extent, typically from 14 to 30% (Fast, 1989) and the starch is gelatinised. The cooking process also affects the texture markedly, the hard grain becoming much softer and more amenable to further processing. Cooking is normally achieved by heating the grain with live steam at temperatures around 120°C.

Chemical reactions also take place during cooking, with changes in the levels of reducing sugars and amino acids of particular interest. These precursors can react, particularly in the toasting stage, to give flavours and colours typical of the Maillard reaction and caramelisation (Kaminski *et al.*, 1981; Anderson *et al.*, 1963). While later processing has a significant effect on final quality, Maillard products are also formed during the cooking stage, along with the destruction of antioxidants (Anderson *et al.*, 1963). Although the Maillard reaction has been well documented in simple amino acid/sugar model systems (Herz & Shallenberger, 1959; Kato *et al.*, 1973; Olsson *et al.*, 1981; Lane, 1983; Ashoor & Zent, 1984; Oh *et al.*, 1991; Tsai *et al.*, 1991), the reactions in cooked wheat take place in a complex matrix which is only partly hydrated and which contains a mixture of sugars and amino acids. Moreover, the conditions change during cooking as the water activity increases, as free amino acids and reducing sugars react and as the pH changes (due to free amino acids). This paper describes the effects of pH, water activity and some inhibitors on the Maillard reaction in a model wheat system under conditions found in commercial cooking processes.

MATERIALS AND METHODS

Wheat samples and standards

Wheat from the 1989 UK harvest was stored in hessian sacks at −5°C to minimise metabolic change. The experiments described in this paper were carried out over a three-month period. Wheat samples were ground when needed using a laboratory mill (Retsch 850407, Stanmore, USA) at low speed using a 0·5 mm sieve.

All laboratory reagents (Analytical grade) were obtained from Sigma (Sigma Chemical Co. Ltd, Poole, UK). The glass ampoules were obtained from Analytical Supplies (Little Eaton, UK).

Preparation of cooked whole wheat grains

Whole wheat grains (200 g) were added to a standard size tin-can which had been perforated with 100 2-mm

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holes. The can was then seamed and heated in a static retort at 121°C for 40 min.

Preparation of ground wheat samples with different initial water activities

Ground wheat (initial a_w = 0·78) was placed on a perforated tray in a sealed plastic container above saturated salt solutions of various water activities (0·16–0·71). The water activity was measured daily and equilibrium occurred after about 6 days. A second set of samples containing sodium metabisulphite (200 mg kg^{-1}) was also prepared.

To prepare samples with an initial water activity greater than 0·71, a different method was used. Ground wheat (25 g) was mixed with 2·5 or 7·5 g of water using a Waring (New Hartford, USA) blender. The samples were then left for 24 h to equilibrate and the water activity measured. A set of samples containing sodium metabisulphite (200 mg kg^{-1}) was also prepared. This method of obtaining high water activities was used to prevent the wheat samples from undergoing microbial damage.

Cooking of the ground wheat samples

Ground wheat samples (2 g) were sealed in glass ampoules (5 ml capacity) under atmospheric conditions and heated in a bench pressure cooker at 103·4 kPa (121·1°C) for 70 min. The ampoules were then left for 24 h so that the final water activities reached equilibrium.

pH analysis

Ground wheat samples (2 g) were added to 50 ml of distilled water and left to stand for 10 min with occasional stirring. The pH was measured before and after cooking with a pH meter.

Water activity measurements

The water activity of the samples were measured using a Decagon Demo CX-1 Series 1/0 (Cambell Scientific, Shepshed, UK) before and after cooking.

Colour measurement

The colour of the cooked wheat samples was measured using a Hunterlab Colour Quest Sphere Spectrocolorimeter Sn C5330 (Virginia, USA) using the L^*, a^* and b^* system. The colorimeter was calibrated with a white tile (L^* = 95·01, a^* = −0·92 and b^* = 0·27), and also a grey tile (L^* = 76·91, a^* = 1·783 and b^* = −0·33) prior to use.

Analysis of free amino acids

Ground wheat (10 g) was added to 25 ml of deionised water and mixed in a Waring blender at top speed for 60 s. The samples were then left to stand for 20 min after which the samples were centrifuged at 15 000 rpm for 10 min. The pH of the extracted supernatant was adjusted to 2 or less by the addition of a 0·1 M sulphosalicylic acid and centrifuged at 40 000 rpm for 30 min. The supernatant was then filtered through a Buchner funnel using Whatman 50 paper. Internal standard (0·4 ml of 1 μM norleucine) was then added to 2 ml of the filtrate and shaken. Samples (50 μl) were then injected into an LKB 4400 Amino Acid Analyser (LKB, Biochrom, Cambridge, UK). The column (270 mm × 4 mm i.d. containing Aminex A9 resin; Biorad, California, USA) was used for the separation of the amino acids.

A sodium citrate buffer system was used (LKB, Cambridge, UK) consisting of 4 buffers:

0·2 M sodium citrate buffer pH 2·65;
0·2 M sodium citrate buffer pH 3·40;
0·2 M sodium citrate buffer pH 4·25;
citrate/borate buffer pH 8·60.

Once separated, the amino acids were derivatised with ninhydrin and detected at 570 nm. Results were integrated (Spectra Physics, SP4100, San Jose, USA) and the total run time of each sample was 2 h.

Analysis of reducing sugars

Reducing sugars were analysed by the method of Ross (1959), but using a Retsch 85040 grinder instead of a blender to homogenise the samples.

Analysis of free lipids

The samples were extracted with chloroform in a Soxhlet apparatus for 7 h. After extraction, the flask was dried to constant weight and this weight was taken as the amount of free lipid.

Analysis of moisture content

Ground wheat samples (10 g) were dried to constant weight at 130°C for 2 h.

Volatile analysis by GC–MS

For GC–MS headspace analysis, the contents of each glass ampoule of cooked ground wheat were placed in a 50 ml screw-top glass jar at room temperature (20 ± 2°C). Volatiles were removed from the headspace with a stream of dry nitrogen (40 ml min^{-1}) into a Tenax trap (SGE, Victoria, Australia) where they were collected for 20 min. The Tenax trap was then desorbed at 220°C from a Unijector (SGE) onto a fused silica capillary column, (BP20; 20 m length × 0·22 mm i.d. × 0·25 μm film thickness (SGE)) and attached to a cryogenic trap (SGE). The column was installed in a Hewlett-Packard gas chromatograph (5890A) (Cheadle Heath, UK) attached to a Hewlett-Packard mass-selective detector (5970).

Helium at 1 ml min^{-1} was used as a carrier gas.

Column temperatures were programmed from 40 to 230°C at 4°C min^{-1} ramp rate. The total run time for each sample was 47·3 min.

Total volatiles were estimated by integrating each chromatogram and taking the sum of the integrated peaks. Linear retention indices were calculated as described by Taylor & Mottram (1990).

Preparation of wheat samples with various initial pH values

Ground wheat (20 g) was mixed with either 0·007, 0·014 or 0·02 g of powdered sodium hydroxide or with 0·008 or 0·02 g of benzoic acid. The samples were then placed on a perforated tray in a sealed plastic container above a saturated salt solution of sodium chloride so that the initial water activities of the samples were approximately the same (0·53).

RESULTS AND DISCUSSION

Effect of cooking on chemical changes in whole wheat

Whole wheat grains were cooked in live steam at 121°C for 40 min so as to imitate a commercial cooking process. They were analysed before and after cooking and the results are shown in Table 1a. During cooking, the levels of free amino acids decreased from 0·19 to 0·14 mg 100 g^{-1} (dry solids basis). A concomitant decrease was also found in the levels of reducing sugars and free lipids which decreased from initial levels of 0·64 and 2·7 mg 100 g^{-1} to 0·53 and 1·8 mg 100 g^{-1} (dry solids basis; 18 and 33% decrease, respectively). The decrease in the levels of free lipids is possibly due to their binding to macromolecules in the wheat matrix. Similar changes have been reported (Arya *et al.*, 1978; Barnes *et al.*, 1981; Addo & Pomeranz, 1991) during the processing of pasta, bread and chapatti when increased proportions of free lipid became bound. Changes also occurred in the water activity and water contents of the grains. The increase in water content from 17·4 to 19·6% was smaller than that noted in a commercial cooking process where the water content increased to 30% (Fast, 1989). A possible reason for this observation may be that, during breakfast cereal manufacture, wheat is semi-crushed (bumped) and cooked in the presence of malt, salt and sucrose, added in an aqueous form, which will affect the water uptake of the cooked wheat. The levels of most free amino acids decreased during cooking (13 to 47%), with a mean fall of around 27% (Table 1b). However, isoleucine, tyrosine and phenylalanine showed increased of 0, 63 and 31%, respectively.

Table 1a. Composition of uncooked and cooked whole wheat

	Uncooked wheat	Cooked wheat
Total free amino acids[a,b]	0·19 ± 0·007	0·14 ± 0·006
Reducing sugars[b]	0·65 ± 0·030	0·53 ± 0·020
Water content[c]	17·40 ± 0·060	19·60 ± 0·090
Water activity	0·78 ± 0·004	0·95 ± 0·017
Free lipid content[b]	2·70 ± 0·100	1·80 ± 0·300

Results are the mean of 3 replicates ± the standard deviations.

[a] Calculated from the amino acid profile in Table 1b (average of 2 determinations).

[b] Results are expressed as g 100 g^{-1} dry weight.

[c] Results are expressed as g 100 g^{-1} wet weight.

Kaminski *et al.* (1981) found that, when malted wheat was heated at 120°C for 45 min in sealed ampoules, the levels of reducing sugars and amino acids also decreased. However, the above author noticed reductions in glutamic acid, tyrosine and lysine in the order 89, 71 and 74%, respectively. These differences may be due to the integrity of the sample as well as the water activity and pH of the model systems.

Model system limitations

Following the initial experiments on whole wheat, experiments were conducted on ground wheat samples sealed in glass ampoules as described in the Materials and Methods section. Ground wheat was used in the model system rather than whole or 'bumped' (semi-crushed) wheat which is more common in commercial systems for a number of reasons. First, grinding wheat facilitates the changes in initial a_w which were a key component of this study. Second, there was concern that a small sample (2 g) of whole wheat which consists of a few grains might show unacceptable variability, whereas a 2 g aliquot of ground wheat sub-sampled from a larger quantity of wheat should be more representative. It is acknowledged that grinding wheat may cause chemical changes, particularly in the lipid components. In addition, commercial cooking takes place in a saturated steam atmosphere, which is practically oxygen-free. The ampoules used in the model systems,

Table 1b. Free amino acids content of uncooked and cooked wheat[a]

Amino acid	Uncooked wheat	Cooked wheat
Aspartic acid	38·4 ± 1·2	33·4 ± 1·1
Threonine	39·8 ± 1·1	23·8 ± 1·0
Serine	8·1 ± 0·3	5·1 ± 0·6
Glutamic acid	22·9 ± 1·0	15·3 ± 1·0
Glycine	12·9 ± 0·4	6·9 ± 0·4
Alanine	23·6 ± 1·2	18·9 ± 0·4
Valine	10·3 ± 0·9	6·5 ± 0·8
Isoleucine	4·1 ± 0·2	4·1 ± 0·2
Leucine	4·5 ± 0·5	2·9 ± 0·3
Tyrosine	3·0 ± 0·1	4·9 ± 0·7
Phenylalanine	2·9 ± 0·3	3·8 ± 0·1
Histidine	4·0 ± 0·2	2·6 ± 0·2
Lysine	2·8 ± 0·1	1·6 ± 0·1
Arginine	13·3 ± 1·1	8·5 ± 0·6
Total	190·6 ± 9·7	138·3 ± 7·5

Results are the average of 2 replicates ± the standard deviation.

[a] Results are expressed as mg 100 g^{-1} dry weight.

however, were not evacuated and so contained air. While the results from the model system indicate trends, they cannot be directly compared to changes in a commercial cooker.

Ground wheat was placed over saturated salt solutions or had water added to produce the appropriate water activity. The values after equilibrium are shown in Table 1a. There was no significant difference in water activity between samples with and without the sodium metabisulphite.

Preliminary experiments

In an attempt to determine the potential of the Maillard reaction during the cooking process, ground wheat was heated in ampoules (initial a_w = 0·78: 121°C, 70 min) with and without the addition of proline and glucose. Proline was chosen as it has been identified as producing cereal-type odours in the Maillard reaction (Hunter *et al.*, 1966; Shigematsu *et al.*, 1975; Saltmarch & Labuza, 1982), and glucose as it is one of the two main reducing monosaccharides in wheat along with fructose (Kent, 1984). The Maillard activity in the samples was estimated by measuring the total area of volatiles produced from each ampoule. The results are presented in Table 2 and, although the variability is high, definite trends can be seen.

Proline and glucose (20 mg of each) produced a total area of around 207 × 10^6 total volatiles in terms of integrator units. Wheat (2 g) produced around 520 × 10^6. In combination, however, wheat/proline/glucose produced about 537 × 10^6 rather than the sum (727 × 10^6) (Table 2). A reason for this much lower level of headspace volatiles may be due to the wheat having a diluting effect on the glucose and proline so limiting their interaction and production of volatiles. These experiments gave an indication of the extent of reaction in wheat and in simple sugar/amino acid systems.

Effect of initial water activity on chemical reaction in heated ground wheat

The Maillard reaction is known to be affected by the prevailing water activity in terms of the rate of reaction and also the products formed (Eichner & Ciner-Dorcik, 1981). In wheat, the initial water content of the stored grain increases from about 14% to around 30% during cooking, corresponding to 0·71 and 0·93 water activity. The Maillard reaction has been reported to produce water (Ames, 1988), to cause a reduction in pH due to loss of basic amino acids (Schroeder *et al.*, 1954; Ellis, 1959) and is known to produce coloured pigments (Wolfrom *et al.*, 1974). It also produces volatile components (Reynolds, 1970; Buckholz, 1988) and all of these parameters were followed in this section.

Table 2. Volatiles produced from cooked ground wheat model systems

Samples			Total volatiles (Integrator Units) × 10^6
Wheat (g)	Proline (mg)	Glucose (mg)	
2	—	—	520 ± 102
—	20	20	207 ± 43
2	20	20	537 ± 75

Results are the means of 3 replicates ± the standard deviation.

Production of water in heated ground-wheat samples

To study the effects of initial water activity on Maillard reactions in wheat, a series of experiments were performed at water activities ranging from 0·14 to 0·90. Ground wheat was held over saturated salt solutions as described in the Materials and Methods section until the required water activity was achieved. Samples were then heated in ampoules and the water activity measured again after cooling and equilibration.

Figure 1 shows the change in water activity after heating ground wheat samples with and without 200 mg kg^{-1} sodium metabisulphite with different initial water activities. Assuming the changes are solely due to the Maillard reaction, the optimum water activity for chemical activity is about 0·45. This is supported by the results of Cheng *et al.* (1985), who found that the highest change in water activity, when milk powder was stored at 55°C for 14 days, occurred at an initial a_w of 0·44. The optimum water activity for the formation of Maillard reaction intermediates was reported to be around 0·5 (Eichner, 1975), which also supports these results.

The samples containing sulphur dioxide are highly comparable with heated wheat alone. Since sulphur dioxide only inhibits the latter stages of the Maillard reaction (Song & Chichester, 1967) and water is formed in the initial stages (Hodge, 1953), this experiment supports the hypothesis that the change in water activity is due to the Maillard reaction. However, when the initial a_w is above 0·85, there is a net loss of water, suggesting that hydration is the major reaction. These

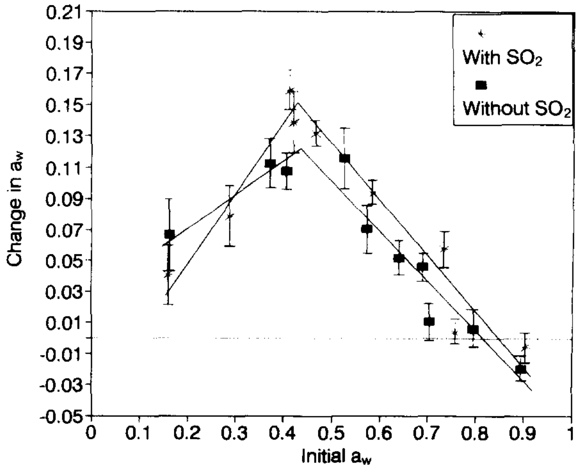

Fig. 1. Effect of initial a_w on change in a_w after heating ground wheat with and without sulphur dioxide. Points represent the mean of 4 replicates ± standard deviation.

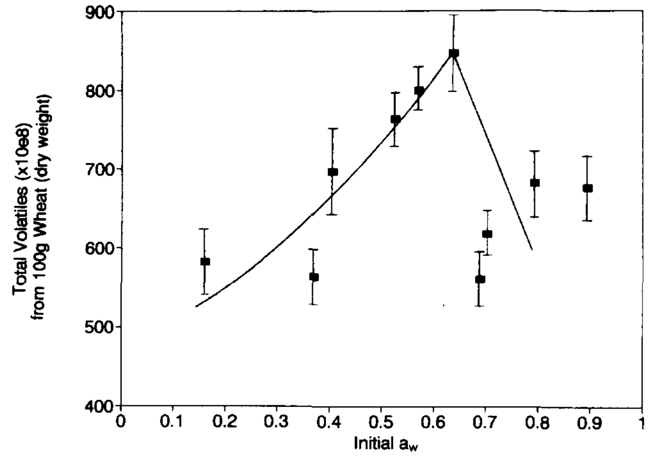

Fig. 2. Effect of initial a_w on total volatile production after heating ground wheat. Points represent the mean of 4 replicates ± standard deviation.

results suggest that two types of reaction are occurring during the heating of wheat, ones that produce water and ones that remove water from the matrix (condensation and hydration reactions).

Effect of initial water activity on volatile production

Experiments were carried out on the heated ground wheat samples with initial water activities between 0·16 and 0·92. After cooling the ampoules, the headspace was collected and chromatographed. Figure 2 shows the effect of initial water activity on total volatile production. The results are not as distinct as those in Fig. 1, which is in part due to variation in the methodology. There does seem to be a maximum production of volatiles at a_w = 0·64.

Qualitative analysis of the volatiles is shown in Table 3 for a_w = 0·64. Figure 1 suggests that the type of reaction changes with water activity and it might be expected that the composition of the volatiles might also change. However, there was considerable inter- and intra-sample variation and it was not possible to detect qualitative changes with changing water activity.

A second set of samples with initial water activities from 0·16 to 0·9 but containing 200 mg kg^{-1} sodium metabisulphite was heated and analysed in the same way. The qualitative analyses are also shown in Table 3. Few of the components in Table 3 are characteristic of the Maillard reaction. These results suggest that, in the cooking of wheat, the Maillard reaction does not contribute significantly to the volatile profile.

Table 3. Compounds identified in the headspace of heated ground wheat at an initial a_w of 0·64

L.R.I. value[a]	GC peak area (%)		Compound
	With SO_2	Without SO_2	
748	3·3	—	Methyl benzene
768	1·2	—	2-Penten-1-ol
786	3·9	1·2	Hexanal
805	0·8	—	2-Furan carboxaldehyde
858	—	0·6	1,2-diethanediol diethyl
868	—	0·6	Hexanol
876	4·1	1·5	Heptan-2-one
889	1·7	1·9	Heptanal
897	1·1	1·1	2,5-dimethyl pyrazine
905	0·9	—	Ethyl pyrazine
908	—	0·9	Unidentified
929	10·2	7·2	Benzaldehyde
935	—	1·1	3,3-dimethyl butan-2-ol
968	1·1	1·4	6 methyl-hept-5-en-2-one
970	12·8	4·6	Oct-1-en-3-ol
975	0·8	1·0	Octan-2-one
981	16·7	21·2	2-Pentyl furan
984	2·2	—	A branched alkane
989	1·3	0·3	Octanal
1001	—	0·6	Decane
1004	1·0	—	Unidentified
1015	—	2·9	Oct-3-en-2-one
1020	2·4	—	2-ethyl hexan-1-ol
1030	—	2·4	Unidentified
1033	0·8	0·6	Unidentified
1058	—	0·5	Octan-1-ol
1060	1·3	—	A branched alkene
1062	—	1·7	A cycloalkane
1083	3·0	—	3,5,5-trimethyl cyclohex-2-en-1-ol
1085	—	6·4	Nonanal
1103	0·8	—	A branched alkane
1165	—	1·1	Nonan-1-ol
1197	—	1·8	Decanal
1278	2·6	2·8	1-(2 hydroxy-5-methyl phenyl) ethanone
1291	0·5	—	A branched alkane
1310	—	0·7	A branched alkane
1324	1·2	—	A branched alkane
1334	—	2·4	Unidentified
1344	1·2	—	Unidentified
1383	0·8	—	An alkene
1398	1·6	1·4	Tetradecane
1421	—	0·6	Unidentified
1498	1·4	2·4	Pentadecane
1597	1·0	—	Hexadecane
1698	—	0·5	Heptadecane

[a] Linear retention indexes.

Effect of initial water activity on colour of heated ground wheat

Ground wheat samples of different initial water activities were heated and the colours of the samples recorded before and after heating. Figure 3 shows the relationship between the L^* values and initial water activity of wheat heated with and without 200 mg kg^{-1} sodium metabisulphite. If the Maillard reaction was entirely responsible for the observed colour, an optimum value might be expected (Lea & Hannan, 1949; Labuza *et al.*, 1970), especially as Fig. 1 demonstrates some type of optimum reaction at a certain water activity. One explanation is that colour development is the result of Maillard and other reactions, for example phenolic and lipid oxidation, and Fig. 3 is a composite of two (or more) reactions.

In an attempt to elucidate the types of reaction occurring, experiments were performed with sulphur dioxide which inhibits both phenolic oxidation (Sayavedra-Soto & Montgomery, 1986; Zawistowski *et al.*, 1987) and later stages of the Maillard reaction (Patton, 1955). Figure 3 suggests that the Maillard reaction and

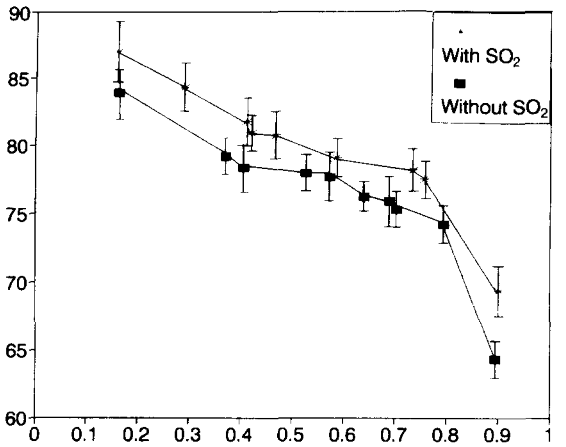

Fig. 3. Effect of initial a_w on colour of wheat heated with and without sulphur dioxide. Points represent the mean of 4 replicates ± standard deviation.

phenolic oxidation play minor roles in the colour formation, as the addition of sulphur dioxide had no effect on the colour of the heated wheat samples.

Effect of pH on the chemical reaction

pH is also known to affect the Maillard reaction (Ashoor & Zent, 1984). Colour formation can either increase as the pH increases, or show an optimum at pH 7, depending upon reaction conditions and substrate (Lea & Hannan, 1949).

Table 4 shows the effect of initial pH on the changes in water activity, pH and colour (L^* value) when ground wheat was heated in the procedure described previously at an initial water activity of 0·45. The pH change increases as initial pH increases from a value of 0·33 at pH 5·62 to 1·42 at pH 8·12. This is in agreement with Schroeder *et al.* (1954) who heated glucose with and without various amino acids in aqueous model systems with varying initial pHs. The Table also shows that there are no noticeable changes in water activity and L^* values with increasing pH. Instead, the a_w fluctuates between 0·13 and 0·16 and the L^* value between 78·4 and 80·0 for all the samples analysed.

Figure 4 shows the volatile production from samples with different initial pHs but with the same initial a_w of 0·53 ± 0·02. Volatile production increases as the initial pH increases to 6·97 and then decreases with increasing pH.

Table 4. Effect of pH on the chemical properties of ground wheat at an initial a_w of 0·45

Initial pH	Final pH	pH change	Increase in a_w	L^* value
5·62 ± 0·01	5·29 ± 0·125	0·33	0·14 ± 0·02	78·4 ± 0·79
6·12 ± 0·01	5·88 ± 0·06	0·24	0·16 ± 0·01	79·5 ± 0·13
6·35 ± 0·02	5·79 ± 0·12	0·56	0·14 ± 0·02	80·0 ± 0·36
6·97 ± 0·05	5·79 ± 0·19	1·18	0·16 ± 0·01	79·4 ± 0·12
7·81 ± 0·04	6·32 ± 0·16	1·49	0·13 ± 0·01	79·6 ± 0·25
8·12 ± 0·03	6·70 ± 0·18	1·42	0·15 ± 0·01	79·6 ± 0·43

Results are the means of 4 replicates ± the standard deviation.

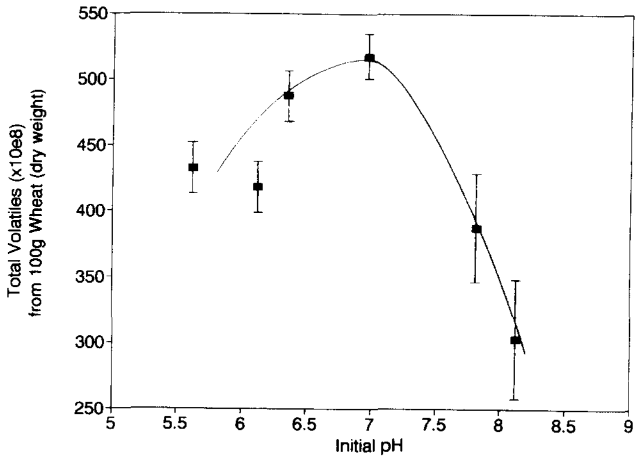

Fig. 4. Effect of initial pH on volatile production after heating ground wheat. Points represent the mean of 4 replicates ± standard deviation.

CONCLUSIONS

The results presented here suggest that the Maillard reaction does occur when wheat is heated. The decrease in levels of reducing sugars and amino acids and the production of water supports this hypothesis. However, there is no direct link between Maillard reaction and colour development in heated wheat, nor with the production of volatiles. Most of the published experiments on the Maillard reaction were performed in simple systems containing two or three reactants (Wolfrom *et al.*, 1974). When ground wheat is used as the reactant system, a large number of reactions and inter-reactions can occur and it is extremely difficult to determine, categorically, the extent of the Maillard reaction.

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