

Effect of pH, Temperature, and Moisture on the Formation of Volatile Compounds in Glycine/Glucose Model Systems

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Mixtures of glycine, glucose, and starch were extrusion cooked using sodium hydroxide at 0, 3, and 6 g/L of extruder water feed, 18% moisture, and 120, 150, and 180 °C target die temperatures, giving extrudates with pH values of 5.6, 6.8, and 7.4. Freeze-dried equimolar solutions of glucose and glycine were heated either dry or after equilibration to ~13% moisture at 180 °C in a reaction-tube system designed to mimic the heating profile in an extruder. Volatile compounds were isolated onto Tenax and analyzed by gas chromatography–mass spectrometry. For the extrudates, total yields of volatiles increased with decreasing pH at 180 °C, reached a maximum at pH 6.8 at 150 °C, and increased with increasing pH at 120 °C. Amounts increased with temperature at all pH values. Pyrazines were the most abundant class for all sets of conditions (54–79% of total volatiles). Pyrroles, ketones, furans, oxazoles, and pyridines were also identified. Yields of volatiles from the reaction-tube samples increased by >60% in the moist system. Levels of individual classes also increased in the presence of moisture, except pyrazines, which decreased ~3.5-fold. Twenty-one of the compounds were common to the reaction-tube samples and the extrudates.

Keywords: Maillard reaction; extrusion cooking; glycine; glucose; pH; temperature; volatiles; modeling

INTRODUCTION

Extrusion cooking of cereals is used extensively in the food industry (1, 2), but the lack of flavor in the resulting products, compared with products obtained by alternative means of processing (e.g., baking or frying), is a serious drawback. The short cooking time encountered during extrusion (usually <1 min) limits the extent of the Maillard reaction, which is primarily responsible for the development of desirable flavor in the foods concerned (3, 4). In addition, flavor compounds are lost to the atmosphere as the product exits the extruder at the die (5). Nevertheless, there have been surprisingly few studies reporting the effects of various processing parameters on the development of volatile compounds during extrusion. Bailey et al. (6) reported on the effect of temperature on volatile compounds in an extruded whey protein concentrate–corn meal mixture. The effect of both moisture and extrusion temperature was investigated with respect to pyrazine formation in potato flakes (7), the formation and degradation of tryptophan Amadori rearrangement products (8), and the formation of volatiles in oat flours (9). Bredie et al. (10) studied the effects of temperature, residence time, and moisture on volatile generation in extruded maize flour, and Ames et al. (11) monitored the effects of temperature and pH on volatiles formed in extruded starch/reducing sugar/cysteine mixtures. Further studies are required

to build up a coherent picture of the effects of extrusion conditions on flavor development.

The use of a simple laboratory apparatus for the small-scale simulation of the conditions encountered during pilot-scale extrusion may aid understanding of the factors affecting chemical reactions under extrusion-like conditions. Several studies have been concerned with the volatile compounds generated by reduced-moisture systems heated at temperatures relevant to food processing, but they were not designed to simulate a specific processing operation, and the temperature profile encountered by the system was not reported (e.g., 12, 13). Other investigations have used apparatus designed to mimic specific food-processing operations. Sensidoni et al. (14) studied the Maillard reaction in an apparatus designed to model the industrial thermal processing of pasta. Vergnes et al. (15) used a capillary rheometer to study starch gelatinization under extrusion-like conditions, and Bates et al. (16) reported the use of a simple apparatus capable of reproducing all of the conditions encountered in an extruder, except shear, to successfully model color development in an extruder. Neither system was suitable for the investigation of the generation of volatile components during extrusion cooking.

The aim of this study was twofold. The first aim was to compare the profiles of volatile compounds from mixtures of glucose/glycine/starch extruded using three different levels of sodium hydroxide in the extruder water feed and three different target die temperatures. The second was to design a heating system capable of mimicking the heating profile of an extruder and to compare the profiles of volatile compounds of a glucose/glycine mixture heated at two moisture levels.

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EXPERIMENTAL PROCEDURES

Materials and Reagents. Glycine (>99%) and D-glucose (99%) were obtained from Sigma Chemical Co. (Poole, U.K.), and soft wheat starch (Abrastarch) was supplied by ABR Foods (Corby, U.K.). The starch had a moisture content of 11.1% (w/w) and a low nitrogen content (<0.15% w/w). Sodium hydroxide was purchased from BDH Chemicals Ltd. (Poole, U.K.). Reaction tubes were freeze-drying ampoules (BDH).

Preparation of Extrudates. Glycine and glucose were premixed with 1 kg of starch, and this mixture was added to more starch in a ribbon blender to give a final concentration of 0.087 mol/kg with respect to both the amino acid and the sugar. These homogeneous feeds were cooked in an APV Baker (Peterborough, U.K.) MPF 50D corotating twin-screw extruder, using a moisture content of 18%, to give expanded products. The extruder was configured to give the following operating conditions: feed rate, 600 g/min; modal residence time, 35 s; screw speed, 350 rpm; target die temperature, 120, 150, or 180 °C. Sodium hydroxide at 0, 3, or 6 g/L of extruder water feed was used to produce extrudates at three pH levels. The temperature within the extruder was monitored using temperature probes situated at intervals along the barrel and at the die. Full experimental details have been reported previously (10, 11, 17). Immediately following preparation, extrudates were ground to powders, packed into polyamide-polyethylene laminate bags (Optivac, Vacuum Packaging International, U.K.), hermetically sealed, and stored at -20 °C for no more than 2 months.

Preparation of Reaction-Tube Samples. *Sample Preparation.* Aqueous solutions, 1 M with respect to both glucose and glycine, were freeze-dried to constant mass. Samples were heated either dry or after equilibration to ~13% moisture ($a_w = 0.77$) over saturated sodium chloride solution.

Heating System. Two heater blocks (80 × 50 × 30 mm) were constructed from aluminum. Three holes were bored into each block. The first (8 mm diameter) was 15 mm along each of the 80 and 30 mm dimensions, to accommodate a glass reaction tube (7 mm external diameter) containing the sample. The second hole was bored close to the first and accommodated a calibrated "k-type" thermocouple. A heating element was placed in the third hole, which was bored 15 mm along the other end of the 80 mm dimension and 15 mm along the 30 mm dimension. Each block was lagged with ceramic tiling and was connected to its own thermostatic control box. The heating profile of the sample tube in each block was obtained, prior to obtaining samples for gas chromatography-mass spectrometry (GC-MS) analysis, by placing the glucose/glycine sample (50 mg) in a reaction tube containing two thermocouples and sealed with Araldite. The first thermocouple was located at the edge of the tube and the second in the center. The temperature recorded by both thermocouples in each block was monitored using chart recorders. The temperature of the first heater block was set at 300 °C, and the second heater block was set at 180 °C.

Glucose/glycine mixtures (50 mg) were placed in reaction tubes that had previously been rinsed in distilled water and dried in a 200 °C oven overnight to remove adsorbed volatiles. Each tube was sealed using an oxyacetylene flame and placed in the first block, preheated to 300 °C. The contents of the tube reached a temperature of 180 °C in 25 ± 2 s, and the tube was then transferred to the second block (transfer time = 0.5 s) for a further 60 s of heating. Following this, the tube was cooled in water at room temperature for 120 s and crushed. The crushed tube and its contents were transferred to the sample flask of the headspace collection apparatus for isolation of the volatile compounds.

pH Measurements. The pH of the extrudates was based on the AOAC method for flour (18). Extrudate (5 g) was mixed with 20 mL of tap water (pH 7.3). After 30 min of constant stirring to give a homogeneous sample, the pH was measured.

Aroma Assessment. Aromas of powdered, dry extrudates (1 g), moistened extrudates (1 g extrudate and ~2.5 mL of distilled water), and heated reaction-tube samples (50 mg and 10 mL of distilled water) in brown glass jars were assessed by

Table 1. Measured Processing Parameters for Glycine/Glucose/Starch Extrudates

target die temp (°C)	NaOH addition (g/L of extruder water feed)	extrudate pH	product temp (°C)	die pressure (MPa)	SME ^a (kJ/kg)
120	0	5.72	126	4.0	783
150	0	5.60	154	4.2	775
180	0	5.76	186	3.0	735
120	3	6.98	119	3.1	602
150	3	6.85	146	2.5	452
180	3	6.62	182	2.0	421
120	6	7.28	116	2.0	589
150	6	7.64	144	2.2	489
180	6	7.36	174	2.1	433

^a Specific mechanical energy.

a panel of five assessors, who were untrained but who were experienced in flavor research. Assessors were free to choose any term they felt was appropriate to describe each sample.

Isolation and GC-MS of Volatile Compounds. Volatile compounds were isolated as described by Ames et al. (11). Briefly, volatiles were isolated from a mixture of either powdered extrudate (10 g) and distilled water (20 mL) or the entire heated reaction-tube sample and distilled water (10 mL) by headspace trapping onto Tenax TA for 1 h at 37 °C. After isolation, the internal standard, 1,2-dichlorobenzene (65 ng in 1 µL of diethyl ether), was injected onto the front end of the Tenax tube immediately prior to GC-MS. Triplicate isolates were prepared for each set of extrusion conditions and reaction-tube samples, and blank isolations were also performed using an empty sample flask. Tenax tubes, containing the isolated volatile compounds, were desorbed onto the front end of a GC column coated with BPX5, prior to GC-MS. All GC-MS conditions of analysis have been reported previously (11). Semiquantitative data were obtained from the mass spectral integration report, with reference to the internal standard. Experimental linear retention indices (LRI) were calculated with reference to the retention times of a series of standard alkanes (C₆-C₂₂), run under the same GC-MS conditions. Compounds were identified as previously described (11) by comparing their mass spectra and LRI values to those for authentic compounds or reported in the literature. When both the MS and LRI data were consistent with those in the literature or obtained for authentic compounds, identities were considered to be positive. When only MS data were available, identities were considered to be tentative.

RESULTS AND DISCUSSION

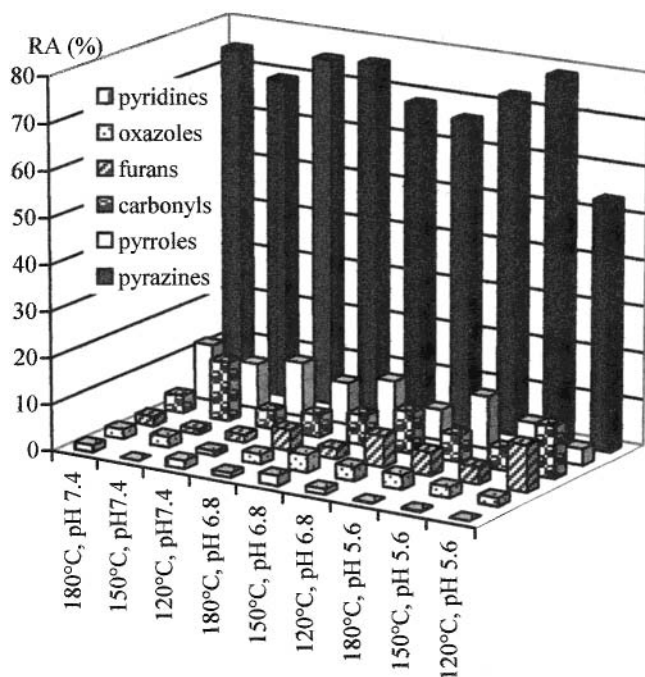
Extrudates. The measured variables for all nine sets of extrusion conditions are shown in Table 1. Specific mechanical energy (SME) values generally decreased with temperature for each pH value and decreased with pH for each temperature setting. Product temperatures were within 6 °C of the corresponding target value. The pH values of the products varied by <0.4 of a pH unit at each level of sodium hydroxide addition.

Aroma Assessment of Extrudates. Around 20 different terms were used to describe the aromas of extrudates (Table 2). The extrudates were more frequently described as "roasted" and "burnt" with increasing sodium hydroxide concentration. Temperature had less of an effect on the perceived aroma.

GC-MS of Extrudates. Fifty-four compounds belonging to six chemical classes, plus three miscellaneous compounds, were identified in the extrudates (Table 3). The relative abundances (RAs) of the classes of compounds at each set of processing conditions are shown in Figure 1. Grand total amounts of compounds increased with decreasing pH at 180 °C, reached a maximum at pH 6.8 at 150 °C, and increased with increasing pH at 120 °C. At each pH value, amounts increased with temper-

Table 2. Aroma Descriptors Applied to Glycine/Glucose/Starch Extrudates

target product temp (°C)	level of NaOH (g/L of extruder water feed)		
	6	3	0
120	bread, roasted, cereal, digestive biscuit, sweet, caramel, acrid, burnt	nutty, popcorn, bread, cereal, biscuit, sweet, burnt baked potato, acrid/sharp, burnt	toasted, caramel, burnt baked potato, acrid, stale, biscuit
150	musty, roasted, cereal, digestive biscuit, sweet, caramel, acrid, burnt	toasted, bread, caramel, malty, milky cereal, biscuit, sweet, burnt baked potato, acrid/sharp, burnt	sweet, milky, burnt baked potato, acrid, biscuit
180	nutty, musty, roasted, cereal, digestive biscuit, sweet, caramel, acrid, burnt	bran, caramel, malty, milky cereal, biscuit, sweet, burnt baked potato, acrid/sharp, burnt	toasted, nutty, shredded wheat, sweet, caramel, biscuit
common terms	roasted, cereal, digestive biscuit, sweet, caramel, acrid, burnt	cereal, biscuit, sweet, burnt baked potato, acrid/sharp, burnt	biscuit

**Figure 1.** Relative abundances of classes of compounds for starch/glycine/glucose extrudates.

ature. Overall, grand total amounts were highest at 180 °C and pH 5.6 and lowest at 120 °C and pH 5.6.

Pyrazines predominated in all extrudates, accounting for 66–79% of the total amounts, except at 120 °C and pH 5.6, when the RA was 54%. Their odors are often described as roasted, nutty, and popcorn (21, 22). The methyl and 2,5(6)-dimethyl compounds were the most abundant derivatives. Many of the pyrazines have been reported previously among the volatile products of heated, reduced-moisture glycine/glucose systems (23–25) or of extruded food systems (7, 9, 10, 26–28). Absolute amounts of pyrazines were an average of ~4.5-fold as high per mole of glucose for these glycine/glucose extrudates compared to products prepared under similar conditions from cysteine, glucose, and starch, when they had RAs of 1–11% (11). Pyrazines are also reported as relatively minor reaction products in a range of aqueous and reduced-moisture glucose/cysteine systems (13, 29–32). This is undoubtedly accounted for in part by the alternative pathways open to glucose degradation products in the cysteine-containing systems, due to the availability of highly reactive sulfur reactants deriving from the cysteine. Arnoldi (33) demonstrated that much lower levels of pyrazines were formed in aqueous cysteine/glucose systems than in mixtures based on lysine. Retroaldolization of the 1- and 3-deoxyglucosones yields carbonyls, including pyruvaldehyde, glyceraldehyde, and glyoxal (34), which may participate in sub-

sequent reactions leading to pyrazines (25, 34) or sulfur compounds (35). Farouk et al. (28) extruded wheat flour with glucose and a single amino acid and showed that, compared to a mixture of wheat flour and glucose extruded without added amino acids, levels of pyrazines increased in all systems except the one containing added cysteine. They concluded that the 93 sulfur-containing heterocycles in their cysteine extrudate were formed from carbonyl precursors that participated in pyrazine formation in systems based on other amino acids (alanine, leucine, lysine, and threonine).

The number of pyrazines was also much higher for the glycine samples, that is, 22 representatives, compared to cysteine (12 compounds) (11). The effects of temperature and pH on the amounts of pyrazines were the same as for totals of all volatile compounds identified in this study (discussed above). Jusino et al. (36) reported that the formation of both methyl- and 2,5-dimethylpyrazine followed a first-order reaction model when a mixture of lysine, glucose, and starch was heated under reduced-moisture conditions at 80–120 °C. Levels of pyrazines are generally considered to increase with temperature and pH (37, 38). The different effects of pH observed at 180 and 150 °C in the current study may be due to the participation of pyrazines in further reactions under the most severe processing conditions (high temperature and high pH), resulting in the formation of nonvolatile products. Yields of pyrazines were suppressed on extrusion of a mixture of autolyzed yeast, glucose, and ammonium bicarbonate, compared to the same mixture without ammonium bicarbonate, and Izzo and Ho (26) hypothesized that this could be due to the Maillard reaction being steered away from pyrazine formation and toward color development.

Pyrroles were the second most abundant class for most sets of extrusion conditions, but amounts were considerably lower than those of pyrazines (RA = 4–12%). Pyrroles are generally less abundant in foods, compared to pyrazines (39), and may contribute cereal notes (21, 22). Yields were always highest at 180 °C, in line with previous studies on extruded systems (9, 10, 40). Most abundant were the methyl and dimethyl derivatives listed in Table 3, and some have previously been identified from a reduced-moisture glycine/glucose system (41). Absolute amounts of pyrroles were ~1.5-fold as high per mole of glucose compared to extrudates prepared from cysteine in place of glycine (11); that is, the effect was much less than for pyrazines. This indicates different formation pathways, suggested mechanisms for pyrrole formation including 3-deoxyglucosone-amino acid interactions (42), and reactions between furans and amino acids (43).

Five carbonyls (all ketones) are listed in Table 3, and several possess buttery, caramel notes (21, 22). Levels

Table 3. Volatile Compounds^a Identified in the Headspace of Starch/Glycine/Glucose Extrudates Prepared at Different Temperature and pH Combinations

class and compound	LRI _{exptl} ^b	LRI _{lit.} ^c	pH 7.4			pH 6.8			pH 5.6		
			180 °C	150 °C	120 °C	180 °C	150 °C	120 °C	180 °C	150 °C	120 °C
carbonyls											
butanone				75	6	64	48	18	63	10	23
2,3-pentanedione	713	702	113	74	8	170	99	21	158	39	15
3-hydroxy-2-butanone	744	737	34		5				91		
2,3-hexanedione	792	790			1	11	2		8		
2-methyl-2-cyclopenten-1-one	920	909									
total carbonyls			147	149	20	245	149	39	321	49	38
furans											
2-ethylfuran	713	705							64	16	
2,5-dimethylfuran	718	707			1				32		
2,3-dimethylfuran	725	715				12			17		
2-methyl-4,5-dihydro-3(2H)-furanone	817	819	8	4	4	30	9	16			
2-furfural	848	848	26		3	68	23	8	109	15	18
2-furanmethanol	876	867	23			103	7		15		
5-methylfurfural	980	976							22		
2-pentylfuran	995	995	26	9		18	11	5	22	9	16
total furans			83	13	8	231	50	29	281	40	34
pyrroles											
1-methyl-1H-pyrrole	749	747	133	63	11	274	110	16	393	62	12
pyrrole	760	756		5						3	
1-ethyl-1H-pyrrole	825	820	22						21		
2,4-dimethylpyrrole	842	843	101	22	14		44	9			
3-methylpyrrole	856	845	15		4		16				
2,5-dimethylpyrrole	872		102	23	22	72	41	3	37	2	
4-ethyl-2-methylpyrrole	951		10		1		3		3		
2-ethyl-3-methylpyrrole	964		10			7	4				
2,3,5-trimethylpyrrole	995				1						
2-formyl-1-methylpyrrole	1022	1027	20		6	63	27	1	100	12	
2-acetyl-1-methylpyrrole	1096		61			40	9		86		
total pyrroles			474	113	59	456	254	29	640	79	12
pyridines											
2-methylpyridine	824	818	6		1	11	7	1	8	2	
2-ethylpyridine	919	903	4								
α-dimethylpyridine	938		20		3	15	26	1			
β-dimethylpyridine	939		27		4	15	17	3			
2,3,5-trimethylpyridine	1076				1						
total pyridines			57	0	9	41	50	5	8	2	0
pyrazines											
pyrazine	750	743	133	63	11	274	110	16	393	62	12
methylpyrazine	839	837	653	238	140	1231	374	97	1127	208	41
2,5(6)-dimethylpyrazine	927	925	749	234	167	1113	482	84	969	145	30
ethylpyrazine	929	928	68	19	7	27	65	9		50	11
2,3-dimethylpyrazine	932	928	393	115	1	425	235	36	543	129	29
vinylpyrazine	947	948	13		2	21	13	2	54	33	3
2-ethyl-6-methylpyrazine	1010	1010	79	12	12	90	123	4	206	38	8
trimethylpyrazine	1014	1014	481	108	13	422	92	31	438	120	38
2-ethyl-5-methylpyrazine	1019	1014	15				21				
2-vinyl-5(6)-methylpyrazine	1037	1034	17			82		3	148	3	
isopropenylpyrazine	1042	1033	5			5			127	39	
2-ethyl-3,5(6)-dimethylpyrazine	1088	1087, 1093	140	8	5	45	11	2	40	9	2
2,5(6)-diethylpyrazine	1089				7				7		
tetramethylpyrazine	1093	1095	11	4	3	28	31	1	19		
2-ethyl-5,6-dimethylpyrazine	1096		54	6	7	81	9	1	31	5	7
2,3-diethylpyrazine	1106		9		1				3	5	
5-methyl-6,7-dihydro-(5H)-cyclopentapyrazine	1163								4		
2,3,5-trimethyl-6-ethylpyrazine	1169		39		1				6		
3,5(6)-diethyl-2-methylpyrazine	1173		22								
2,5-dimethyl-3-isopropylpyrazine	1177								6		
2-ethyl-6,7-dihydro-(5H)-cyclopentapyrazine	1196		6						5		
5-methylquinoxaline	1344								2		
total pyrazines			2887	807	377	3844	1566	286	4128	846	181

Table 3. (Continued)

class and compound	LRI _{exptl} ^b	LRI _{lit.} ^c	pH 7.4			pH 6.8			pH 5.6		
			180 °C	150 °C	120 °C	180 °C	150 °C	120 °C	180 °C	150 °C	120 °C
oxazoles											
4,5-dimethyloxazole	761		64	27	1	90	63	11	142	22	5
2,4-dimethyloxazole	783		3			16	11	2	21	4	1
trimethyloxazole	850	858	14		2		12		14		
total oxazoles			81	27	3	106	86	13	177	26	6
miscellaneous											
hexanal	810	809	118	53	19	120	103	27	100	34	66
hexanenitrile	881	880	9		2	11	13	1	6		
limonene	1034	1033	21	5	6	34	18	2			
total miscellaneous			148	58	27	165	134	30	106	34	66
grand total			3877	1167	503	5088	2289	431	5661	1076	337

^a Amounts of compounds are quoted in ng/10 g of extrudate. Figures quoted are the means of triplicate analyses. ^b Calculated linear retention indices for identified compounds. ^c Linear retention indices obtained for authentic compounds analyzed on the same GC column or from the literature (19, 20). Values for authentic compounds are in italics.

of carbonyls were, on average, 8-fold as great per mole of glucose in glycine/glucose extrudates compared to the cysteine/glucose products. This was mainly due to the much higher levels of 2,3-pentanedione in the glycine samples; this compound was identified only in the 180 °C, pH 7.5, material prepared using cysteine. 2,3-Pentanedione is a precursor of 2-mercapto-3-pentanone and 3-mercapto-2-pentanone (44), identified in the cysteine extrudates (11), and these compounds may oxidize to yield their corresponding mono-, di-, and trisulfides (44), as well as reacting further, for example, with ammonia and aldehydes to give thiazoles (45). During extrusion of the glycine samples, such routes are not available and reaction pathways available to 2,3-pentanedione are limited to, for example, Strecker degradation and condensation of the resulting α -aminoketone to yield pyrazines, with methyl and ethyl substituents at positions 2 and 3, for example, 2-ethyl-3,5(6)-dimethylpyrazine and 3,5(6)-diethyl-2-methylpyrazine reported in Table 3.

With the exception of 2-pentylfuran (formed from trace lipid in the starch), all of the furans listed in Table 3 come from the glucose. The odors of several have been described as sweet and caramel-like (21, 22). 2-Furfural was a major component and was formed in increasing amounts both with decreasing pH and with increasing temperature, in line with the literature (46). It has been reported from an aqueous glucose/glycine system (47). 2-Furanmethanol was also prominent in most systems in which furfural was identified. Levels of furans were about the same in extrudates prepared using both glycine and cysteine, but furfural was more abundant in the glycine samples.

Three oxazoles were identified and, on average, levels of this class were about half of those in the cysteine samples. Total levels of pyridines were about the same for extrudates prepared from glycine or cysteine.

Reaction-Tube Samples. One aim of this study was to produce a heating system that could be used for the laboratory-scale study of the development of volatile compounds in amino acid/sugar mixtures of reduced-moisture content. Of particular interest was the ability of such a system to mimic the formation of components responsible for flavor in materials produced using a pilot-plant extruder. The heating profiles of the heater-block system and the extruder, operated using a residence time of 60 s and a target die temperature of

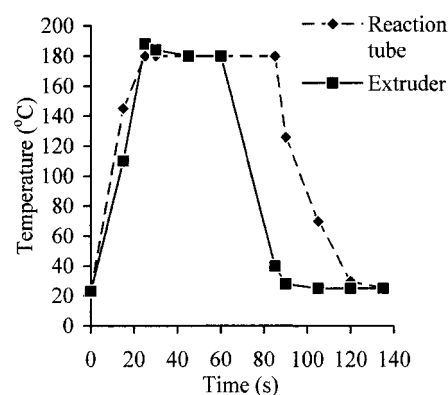


Figure 2. Heating profiles for the heating block system and the extruder.

180 °C, are shown in Figure 2. The data shown are the means of four replicate experiments, and the sample took 25 ± 2 s to reach 180 °C in the first heater block (set at 180 °C). The temperature profiles in the center and at the edge of the reaction tubes were virtually the same. The rates of heating in the extruder and reaction tubes were almost identical, and the rates of cooling were very similar. The heater block system was simple to operate and showed very small variation in heating profile among tubes.

Aroma Assessment of Reaction-Tube Samples. After heating, the 13% moisture sample was described as "burnt toast", "acid", "slightly nutty", and "biscuity". The terms "burnt caramel", "burnt toast", and "slightly biscuity" were applied to the dry sample.

GC-MS of Reaction-Tube Samples. The volatile compounds identified from mixtures of glycine and glucose heated without added water and equilibrated to 0.77 a_w , ~13% moisture, are shown in Table 4. The total amount of volatiles increased by >60% in the presence of water, and absolute levels of all compound classes also increased, except for pyrazines, which decreased ~3.5-fold. The percent RA values for each class of compounds are depicted in Figure 3. In the absence of added water, pyrazines were the most abundant class (RA = 50.4%), and the furans were second most abundant at 36.4%. In contrast, when the water activity was adjusted to 0.77, furans predominated at 82.2% and pyrazines comprised only 8.8% of the total aroma isolate. The different proportions of pyrazines and

Table 4. Volatile Compounds^a Identified in the Headspace of a Glycine/Glucose System Processed in a Model Heater

class and compound	LRI _{exptl} ^b	LRI _{lit.} ^c	without water	with water
carbonyls				
butanone			40	
2,3-pentanedione	713	702	87	260
3,4-hexanedione	816	796	92	184
4-methyl-3-penten-2-one	891			318
2-cyclopenten-1,4-dione	911	907	167	974
2-methyl-2-cyclopenten-1-one	925	909	853	490
total carbonyls			1239	2226
furans				
2-methyl-5-ethylfuran	803		26	
2,3,5-trimethylfuran	817		17	
2-vinyl-5-methylfuran	841		144	782
2-furfural	852	848	589	8938
2-(2-propenyl)furan	862	864	80	
2-furanmethanol	880	867	231	423
2-methyl-5-propenylfuran	972		359	417
5-methylfurfural	990	976	11464	41552
2-propionylfuran	1030	1016	241	236
1-(2-furyl)-2-propanone	1064		323	199
1-(2-furyl)-3-butanone	1089	1089	83	167
2-methylbenzofuran	1131	1127	73	206
1-(5-methyl-2-furyl)-1-propanone	1159	1145	120	
5-methyl-2-furfurylfuran	1195		484	500
2,2'-methylenebis(5-methyl)furan	1290		455	1137
total furans			14689	54557
pyrroles				
1-methyl-1 <i>H</i> -pyrrole	769	747	174	
2,5-dimethyl-1-ethylpyrrole	942		68	
2-formyl-1-methylpyrrole	1022	1027	626	690
2-acetylpyrrole	1095	1087	285	582
2-acetyl-1-methylpyrrole	1100		2247	2489
total pyrroles			3400	3761
pyridines				
2-acetylpyridine	1057	1050	511	
total pyridines			511	
pyrazines				
methylpyrazine	839	837	243	723
2,3-dimethylpyrazine	940	928	1748	618
2-ethyl-5(6)-methylpyrazine	1015	1010, 1014	2086	785
trimethylpyrazine	1021	1014	9915	2546
2-vinyl-5(6)-methylpyrazine	1034	1034	315	97
2-ethyl-3,6-dimethylpyrazine	1091	1087	215	582
2-ethyl-3,5-dimethylpyrazine	1092	1093	3147	168
2-ethyl-5,6-dimethylpyrazine	1096		1039	
3,5-diethyl-2-methylpyrazine	1172		473	186
3,6-diethyl-2-methylpyrazine	1177		203	
2-ethyl-6,7-dihydro-(5 <i>H</i>)-cyclopentapyrazine	1202		229	132
2-butyl-3-methylpyrazine	1213		91	
2(3),5-dimethyl-6,7-dihydro-(5 <i>H</i>)-cyclopentapyrazine	1220		58	
3(2),5-dimethyl-6,7-dihydro-(5 <i>H</i>)-cyclopentapyrazine	1243		311	
5,7-dimethyl-5,6,7,8-tetramethylquinoxaline	1264		26	
2,3,5-trimethyl-5,7-dihydro-(5 <i>H</i>)-cyclopentapyrazine	1270		101	
2-propyl-3,5,6-trimethylpyrazine	1280		84	
2-(2'-furyl)-5(or 6)-methylpyrazine	1381		66	
total pyrazines			20350	5837
oxazoles				
trimethyloxazole	853	858	197	
total oxazoles			197	
grand total			40386	66381

^a Amounts of compounds are quoted in ng/50 mg of reaction mixture. Figures quoted are the means of triplicate analyses. ^b Calculated linear retention indices for identified compounds. ^c Linear retention indices obtained for authentic compounds analyzed on the same GC column or from the literature (19, 20). Values for authentic compounds are in italics.

furans in the two systems had very little influence on the perceived odor of the heated reaction-tube samples.

Fifteen furans were identified. The most abundant compound in both systems was 5-methylfurfural, and

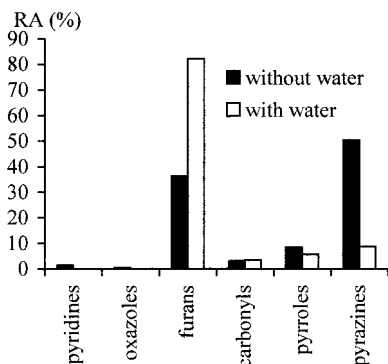


Figure 3. Relative abundances of classes of volatile compounds for a glycine/glucose model system heated dry and with 13% water.

it increased ~3.5-fold in the presence of water to 83 μg /0.1 g of reaction mixture. It forms by dehydration of the 3-deoxyglucosone (48). The second most abundant furan was 2-furfural, and amounts increased 15-fold in the water-containing system. Other furans were less affected by the presence of water or were identified only in the dry system, for example, 1-(5-methyl-2-furanyl)-1-propanone. Yields of furfural from extruded oat flours increased on decreasing moisture from 18 to 14.5% (9). However, both moisture levels were higher than that of the moist system in the present study. Also, starch and pentosans are potential sources of 2-furfural in oat flours, in addition to sugars.

Eighteen pyrazines are listed in Table 4, but only nine of them were identified in the moist system. Potato flakes extruded at 160 °C and at moisture levels of 25–48% showed increased yields of pyrazines with decreasing moisture, especially between 38 and 25% water, when the total pyrazine yield increased from 2.7 to 51.4 ppm (7). Oat flours extruded at 14.5 and 18% moisture and at two temperatures (150 and 180 °C) showed consistent increases in pyrazine yields at the lower moisture level (9).

Levels of most aliphatic carbonyls increased in the presence of water. The three pyrroles containing carbonyl functions increased slightly with moisture, whereas the two compounds possessing only alkyl substituents were identified solely in the dry system. One pyridine and one oxazole were identified, but only in the dry system.

The reaction-tube system was successful in heating the glycine/glucose mixture to a temperature and for a time comparable to the conditions encountered during extrusion cooking of foods. The reaction system samples were heated at 180 °C for much longer (60 s) than the residence time (35 s) used to prepare the extrudates for the data in Table 3. In addition, the reaction-tube systems experienced no shear and different pressure effects, were of lower moisture content than the extrudates described in Table 3, and contained no starch. Therefore, a detailed comparison of the data from the two systems is not justified. Nevertheless, of the 46 compounds identified from the reaction-tube systems, 21 also feature in Table 3. Such a laboratory heating system is versatile and may easily be adapted to model more closely specific extrusion conditions (residence time, moisture content, and incorporation of starch) to give guidance to the food technologist on the relationships between specific heating conditions and system

composition and the profile of volatile reaction products.

In conclusion, total amounts of compounds increased with temperature at each pH value. The effects of pH in the range 5.6–7.4 were different at each temperature: yields increased with decreasing pH at 180 °C, reached a maximum at pH 6.8 at 150 °C, and increased with increasing pH at 120 °C. Pyrazines dominated in all systems (RA = 54–79%). The reaction-tube system showed promise for modeling on a small scale the development of volatile compounds during extrusion. Yields of all classes, except pyrazines, increased in the presence of moisture; pyrazines decreased ~3.5-fold.

ABBREVIATIONS USED

GC-MS, gas chromatography–mass spectrometry; RA, relative abundance; SME, specific mechanical energy.

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