### ANALYSIS OF AROMA VOLATILES GENERATED DURING THE EXTRUSION OF MAIZE FLOUR USING SOLID PHASE MICRO – EXTRACTION (SPME)

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#### ABSTRACT

Volatile components in extruded maize flour at 140°C were extracted by Solid Phase Micro – Extraction (SPME), identified and evaluated by GC – MS. More than 90 compounds were successfully detected. Among the flavor active volatiles, pyrazines were the most prominent class of compounds, especially the alkyl substituted derivatives, followed by furans. Few pyrroles and sulfur – compounds were also identified. The above classes are highly contributed to the overall flavor, in spite of their relatively low amounts which may be due to the low extrusion temperature. Aldehydes, fatty acids, ketones, hydrocarbons and other aliphatic derivatives contributed only a little to the resulting flavor in contrast to their amounts among the identified volatiles. Maillard reactions as well as lipid degradation are the main reasons for the formation of these volatiles. The browning reaction is only moderate, the increase of a\* (redness –positive- to greenness –negative) and b\* (yellowness –positive- to blueness – negative) corresponds to the increase in redness and yellowness, respectively, which occurs in the beginning of non-enzymatic browning. Sensory characteristics of the extruded maize flour could be easily correlated with the identified compounds.

Key words: aroma volatiles, color, extrusion, flavor, maize flour, sensory, SPME.

#### **1. INTRODUCTION**

The extrusion cooking has become a favorite alternative for baking, particularly for the technological processing of cereals and starchy foods into a variety of food products (Huber, 1991) The extrusion conditions reduced the requirements for energy as well as the moisture content in comparison to baking technique which may lead to damage by microorganisms during storage. During extrusion, raw materials exposed to high temperature, pressure and shear force to mix and cause chemical changes which constitute cooking.

These chemical changes, among many others, involve the production of flavors which give the final product its characteristics. These flavor compounds may be originated from a number of compounds in the starting material and through a number of different reactions including lipid oxidation. breakdown of carotenoids, deamidation of glutamine and asparagines and the formation of Maillard reaction products (Riha and Ho, 1998). Analysis of flavor volatile compounds produced during extrusion of ground malt (Fors and Eriksson, 1986), potato flakes (Maga and Sizer, 1979) and semolina (Farouk et al., 2000; Farouk et al., 2001), showed the

effects of different extrusion conditions on the yield of pyrazines.

Pyrazines which are one of the classes responsible for the toasted and nutty extrudate flavor, may be originated from the proteins and carbohydrates found in flours. During extrusion of oat flour, compounds such as 2,4-decadienal and 2,4-nonadienal were detected due to lipid degradation as well as vanillin which may be due to phenol content of the flour (Guth and Grosch, 1993).

One of the most important raw materials for extrusion cooking is corn meal, which is transformed into extrudates of interesting flavor character (Chen et al., 1991). The main advantage of corn processing is time, energy and cost saving. The volatiles produced from an extruded corn - based model system has been studied by Ho et al . (1989) using single screw extruder at 120°C - 165°C. The extruded samples were ground and extracted with diethyl ether, the volatiles were analyzed by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC / MS). Another study on flavor production during corn flour extrusion was performed using twin - screw extruder at 178°C (Nair et al., 1994). Volatiles were collected

using cold-trap, analyzed by GC / MS, but surprisingly without any kind of quantification. A drawback of extruded products is their weaker aroma and flavor intensity than that of traditional bakery products (Pokorny *et al.*, 2002). Recent developments in the methods of isolation and measurement of volatiles should be exploitive, especially supercritical fluid and SPME which have not yet been fully evaluated for cereals. However, SPME is nowadays accepted as a simple and powerful tool for solving many analytical problems (Pawliszyn, 1997).

The present study aimed to characterize the volatile aroma compounds using SPME in the extrusion cooking of maize flour at standard industrial conditions and normal moisture content, as well as the sensory evaluation of the final product.

# 2. MATERIALS AND METHODS

# 2.1. Source of maize flour

Maize flour was obtained from Azteca Milling L. B., (Edinburgh, Texas, USA), Type CHIP DELIGHT #6 YELLOW. It contained 12.0% moisture, 1.0% ash, 8.2% protein and 3.5% fat.

# 2.2. Extrusion process

The material (5 Kg.) was thoroughly sieved and then fed to the extruder (single – screw collet VUMPP-83, CR; screw type: 3-way; distance between flights: 36mm; screw rotation: 5.85Hz; dosing: 1.923; feed rate: only in the feed zone, defined by dosing; residence time: 30s; the maximum extrusion temperature: 140°C; dosing: 40Kg/h; shaping dies: diameter of 12mm; distance dies: diameter of 88mm; die temperature: 110°C). The extruded samples were immediately crushed and stored at room temperature in ground glass bottles filled up to the neck.

# 2.3. Extraction of volatiles

The SPME procedure was used (Farouk *et al.*, 2001). A Carboxen<sup>TM</sup> / Polydimethylsiloxane (PDMS) 75µm fibre for manual holder was produced by Supelco (Bellefonte, CA, USA). The extraction time was 1 Hour at 85°C, and the desorption time was 2 min at 220°C. The fibre was then cleaned for 30 min at 220°C before extracting the next sample. The procedure is affected by the extraction conditions due to which, these were carefully controlled. The results apply, nevertheless, solely to the sample analyzed, and to the solid phase used for extraction.

### 2.4. Gas Chromatography/Mass Spectrometric analysis (GC / MS)

The obtained volatiles were analyzed using GC-MS apparatus. Separation was performed on Thermo gas chromatograph (Walnut creek, California, USA) equipped with Finnigan mat SSQ 7000 mass spectrometer and a 60m x 0.32mm DB-wax capillary column (J&W, USA). The column temperature was programmed from 50°C (isothermal for 2 min.) to 220°C at a rate of 2°C / min with 30 min. isothermal hold. The injector temperature was 220°C and the transition line temperature was 220°C. The carrier gas was helium and the column pressure head was 10-15psi. The mass spectrometer had a scan range from m/z 33 to m/z 300. Ionization energy was set at 70eV. Identification of compounds was based on the comparison with the MS computer library (NIST and Wiley software package, ThermoFinnigan) and published spectra. A linear retention index was calculated for each compound using the retention times of a homologous series of C6 - C26 nalkanes.

# 2.5. Color evaluation

The extrudate sample was finely ground for 30s in a Moulinex processor (Moulinex, France). A CCD fiber optic spectrophotometer S 200 (Ocean Optic. Ltd., FL, USA) was used for measuring the reflected light. A standard light source D65 was used; the reflexion assembly probe consisted of 7 fibers in a ferrule. The results were processed by the software version 3.1. The Spectrawin following parameters were measured: L\* -expressed the lightness (in %); the a\* value – redness (positive) to greenness (negative); b\* value - the yellowness (positive) to blueness (negative); the hue angle  $h^*$  is defined as  $\tan^{-1} b^* / a^*$ ; the chroma  $c^* = (a^{*2} + b^{*2})^{0.5}$ ; the color difference:  $\Delta \mathbf{E} = (\Delta \mathbf{a}^{*2} + \Delta \mathbf{b}^{*2} + \Delta \mathbf{L}^{*2})^{0.5}.$ 

# 2.6. Sensory analysis

The sensory analysis was carried out under the conditions specified by the international standards (ISO); general guidelines after ISO 6658-1985; unstructured graphical scales (ISO 4121.2-1988) were presented as straight lines 70mm long, provided with descriptors on either ends (intensity of brown coloration: 0 mm=very light, 70 mm=very dark; pleasantness of odor: 0 mm=very unpleasant, 70 mm=very pleasant; odor intensity: 0 mm= imperceptible, 70 mm=very strong; texture (assessed by pressing the sample between fingers): 0mm=greasy, 70 mm=fragile). The sensory profile is based on free choice profiling, and the following descriptors were retained out of 32 collected descriptors (Farouk et al., 2000; Farouk et al., 2001): 1= roasted, bread crust, roasted peanuts,

ginger bread; 2= burnt, caramel, bitter; 3= woody, peel, rubbery; 4=after dough, floury, bread crumb; 5= spicy, sulphur, after onion, garlic; 6= sharp, pungent, penetrating; 7= fatty, oily, buttery; 8= earthy, musty, after earthy, moldy, after sweat, wet dog: 9= malty, cocoa 10= solvents, synthetics, powder, sweet; chemicals; 11= others. The profile evaluation of the descriptors range from 0 mm = absent, 70mm = very strong. The colour intensity and the colour hue were assessed under standard light source C (CIE, corresponding to the spectrum of sun surface ). Odour profiles are tested by sniffing from ground wide - neck 500ml. glass bottles.

# **3. RESULTS AND DISCUSSION**

The identified compounds of the volatile fraction are shown in Table (1) and Figure (1). Ninetv-three compounds were recorded. including 19 pyrazines, 10 furans, 9 aliphatic alcohols, 9 aliphatic carboxylic acids, 7 aliphatic aldehydes, 6 pyrroles, 6 sulfur - containing compounds, 6 aliphatic hydrocarbons, 5 aliphatic ketones and 1 pyridine. The quantitative distribution of different classes of compounds showed that, aliphatic aldehydes are predominant (20.85%), followed by pyrazines (17.98%) and aliphatic carboxylic acids (16.80%), while the sulfur-containing is the least detected group with 0.90%.

Only about 80 compounds were identified by Bredie et al. (1998 a & b) in eight maize extrudates treated at different conditions, among them 40 compounds at 120°C and 150°C with different moisture content. While a smaller number could be detected by Ho et al. (1989) at 120 °C. In another interesting study, Nair et al. (1994) recovered less than 50 compounds from extrudate and detected about 70 volatiles released at the die, but unfortunately, they did not quantify them. In the discussion concerning the composition of volatiles, it should be made clear that, the results depend on the extraction method. In the case of the SPME method, it depends on properties of the film on the fibre surfaces, which is carboxen in the present study.

Pyrazines are one of the most important classes identified in the extrudate. The derivatives of pyrazines detected, were common to other extruded cereals and to many heat – processed foods and model systems (Maga, 1992). Methyl pyrazine, dimethyl pyrazines and ethyl dimethyl pyrazines were previously reported in other studies (Ho *et al.*, 1989; Bredie *et al.*, 1998 a & b), however, most of the rest pyrazines detected in the extrudate, were not

identified before under the same extrusion temperature, including derivatives with higher concentrations e.g. trimethyl pyrazine (1.29 %) and vinylmethyl pyrazines (1.29 %). Generally, pyrazines are formed in the reaction of an aminogroup with carbonyl group during Maillard browning reaction (Hwang et al., 1994 a & b). Proteins, peptides and amino acids, present as natural components in maize flour, were obviously sufficient for the pyrazine formation. The amount of ammonia, necessary for the pyrazine formation can be liberated not only by the cleavage of the peptide bond, but also by deamidation of glutamine and asparagines bound in proteins (Zhang, 1994). Additionally, Maillard reaction may occur even if no reducing sugar is added to the feed, since starch and fiber fragments can react (Camire, 1998). Most of the pyrazines identified in the extrudate, consisted of methyl- and methylethyl substituted derivatives which provide a roasted and toasted flavor note (Maga, 1992). They were reported among pyrazines from crust of white American bread (Sizer et al., 1975). However, vinyl and acetyl derivatives here identified are in agreement with those formed in extruded malt, which also contain reducing sugars (Fors and Eriksson, 1986).

Ten furans were identified in the extrudate, only pentyl furan, furfural and furanmethanol were reported before, while the rest are not. Furans are oxygen-containing heterocycles that provide a sweet, or caramel - like aroma and may be formed from pyrolysis of sugars (Fors, 1983). During extrusion, the branched structure of amylopectin branches is susceptible to shear. Both amylose and amylopectin molecules may decrease in molecular weight. Politz et al. (1994) studied relative molecular weight distribution in extruded corn flour containing 60% amylopectin. Large amylopectin molecules were more likely to degrade. This molecular degradation may be exploited produce dextrins to and monosaccharides (glucose) which may be the main furan source.

The two thiophenes identified in the extrudate, namely 2-hexyl thiophene (0.14%) and 2-thiophene carboxaldehyde (0.01%) are not reported before during extrusion at the same conditions. Thiophenes are sulfur – containing compounds which have been previously reported in cooked meat and are generally responsible for a mild sulfurous odor (Shibamoto, 1980). Shibamoto (1977) concluded that, thiophenes were formed from the reaction of a sugar or carbohydrate with hydrogen sulfide or an amino acid. 2-Formyl thiophene may be produced

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No	(1). Volatile compounds identified in the extruded mai	D4	DI	A mag 0/
1	Compound	<b>KI.</b>	<b>KI</b>	Area %
1	Decene	6.720	907	0.83
2	Decale Decale	0.729	1000	1.24
3	Benzene, 2-methylpropyl-	0.772	1007	1.19
4		8./03 10.291	1090	17.34
5	p-Aylene	10.381	1133	0.45
6	I-Butanol Hertenel	11.606	1138	0.33
/	Heptanal	11.840	1170	0.62
8	Decane, 2,4(3,6)-dimethyl-	11.965	11/8	1.28
9	d-Limonene	12.107	1181	3.01
10	Undecane, 4-methyl-	12.290	1184	6.30
11	Pyrazine	12.807	1194	0.11
12	Furan, 2-pentyl-	13.516	1217	1.17
13	2-Methylthiazole	13.691	1240	0.03
14	1-Pentanol	13.966	1242	1.82
15	Thiazole	14.091	1249	0.04
16	Pyrazine, 2-methyl-	14.608	1257	2.28
17	Benzene, 1-methyl-4-(1-methylethyl)-	14.842	1261	0.12
18	Benzene, 1,3,5-trimethyl-	15.250	1283	0.18
19	2-Pentanol, 4-methyl-	15.400	1286	0.21
20	Tridecane	15.684	1300	5.96
21	Acetic acid, methyl ester	15.942	1302	0.96
22	Pyrazine, 2,5-dimethyl-	16.526	1315	4.27
23	Pyrazine, 2,6-dimethyl-	16.743	1322	5.32
24	Pyrazine, ethyl-	16.968	1325	0.17
25	Pyrazine, 2,3-dimethyl-	17.376	1336	0.13
26	1-Hexanol	17.526	1354	0.51
27	2-Isopropyl-5-methyl-hex-2-enal	17.952	1362	1.11
28	Pyrazine, 2-ethyl-6-methyl-	18.735	1378	0.29
29	Dimethyltrisulfide	18.769	1379	0.63
30	Pyrazine, 2-ethyl-5-methyl-	18.952	1384	0.66
31	Pyrazine, trimethyl-	19.336	1397	1.29
32	Pyrazine, 2-ethyl-3-methyl-	19.419	1403	0.41
33	3-Octen-2-one	19.586	1406	0.35
34	1,3-Hexadiene, 3-ethyl-4-methyl-	19.953	1412	0.53
35	Pyrazine, 2-vinyl-	20.628	1422	0.10
36	Benzene, 1-ethenyl-3(4)-ethyl-	20.661	1425	0.47
37	Pyrazine, 3-ethyl-2,5-dimethyl-	20.761	1435	1.16
38	7-Octen-4-ol	20.936	1438	0.82
39	1-Hexanol, 3(5)-methyl-	21.095	1442	0.29
40	Acetic acid	21.337	1448	0.02
41	2-Furfural	21.662	1461	0.13
42	1-Hexanol, 2-ethyl-	22.295	1471	0.37
43	Pyrazine, 2-vinyl-6-methyl-	22.370	1473	0.87
44	Pyrazine, 2-vinyl-5-methyl-	22.587	1476	0.42
45	Decanal	22.704	1484	0.36
46	Ethanone, 1-(2-furanyl)-	23.029	1487	0.19
47	3.5-Octadien-2-one	23.429	1498	0.18
48	Benzaldehyde	23.679	1505	3.86

Table (1): Volatile compounds identified in the extruded maize flour.

Cont., Table (1):Volatile compounds identified in the extruded maize flour.						
49	2-Nonenal	23.963	1510	0.43		
50	1-Octanol	24.538	1530	0.58		
51	Thiophene, 2-hexyl-	24.863	1544	0.14		
52	3,5-Octadien-2-one	25.113	1555	0.21		
53	2-Furancarboxaldehyde, 5-methyl-	25.297	1562	0.06		
54	Pentadecane, 2-methyl-	25.847	1575	0.22		
55	Ethanone, 1-(2-pyridinyl)-	26.239	1585	0.16		
56	2-Octen-1-ol	26.431	1592	0.05		
57	2-Methyl-3-propylpyrazine	26.689	1601	0.06		
58	Acetylpyrazine	26.989	1611	0.43		
59	Butyrlactone	27.198	1624	2.30		
60	2-Acetylthiazole	27.665	1641	0.05		
61	Acetophenone	27.806	1646	0.76		
62	2-Furanmethanol	27.956	1651	0.12		
63	6,7-Dodecanedione	28.031	1654	0.54		
64	2-Pyrrolidone, 1-methyl-	28.306	1666	0.06		
65	1-(5-Methyl-2-pyrazinyl)-1-ethanone	28.748	1675	0.17		
66	1-(6-Methyl-2-pyrazinyl)-1-ethanone	29.040	1684	0.19		
67	3-Thiophenecarboxaldehyde	29.198	1687	0.01		
68	2-Methyldihydrocyclopentapyrazine	29.599	1707	0.08		
69	Pentanoic acid	30.482	1736	0.60		
70	Pentanoic acid, 4-methyl-	32.433	1756	0.14		
71	2,4-Decadienal	32.575	1758	0.14		
72	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	33.033	1793	1.32		
73	Hexanoic acid	33.600	1847	9.19		
74	1-(5-Methyl-2-furanyl)-1,2-propandione	34.067	1852	0.01		
75	Benzyl alcohol	34.492	1873	0.18		
76	Butylatedhydroxytoluene	35.468	1922	0.32		
77	2(3H)-furanone, 5-butyldihydro-	35.743	1936	0.10		
78	Hexanoic acid, 2-ethyl-	36.493	1947	0.26		
79	Heptanoic acid	36.627	1950	0.82		
80	Maltol	36.927	1954	0.16		
81	Ethanone, 1-(1H-pyrrol-2-yl)-	37.160	1956	0.24		
82	Phenol	38.127	1997	0.61		
83	1H-Pyrrole-2-carboxaldehyde	38.677	2008	0.11		
84	2-Pyrrolidinone	38.811	2010	0.27		
85	Benzofuran, 7(2)-methyl-	39.136	2014	0.96		
86	Octanoic acid	39.469	2019	4.16		
87	1-Pyrrolidinecarboxaldehyde	41.242	2099	0.07		
88	Nonanoic acid	42.209	2144	0.83		
89	4-Hydroxy-2-methylacetophenone	43.068	2183	0.24		
90	Decanoic acid	44.810	2262	0.57		
91	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	45.327	2286	1.36		
92	Benzofuran, 2,3-dihydro-	48.137	2388	0.29		
93	Indole	49.938	2454	0.03		

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Figure (1): Gas chromatogram of volatiles isolated from extruded maize flour

from the reaction of furfural, hydrogen sulfide and ammonia during extrusion, while long – chain alkyl thiophenes may be formed by the reaction of hydrogen sulfide or ammonia with alkadienals (Farmer *et al.*, 1989).

The flavor characteristics of thiazoles have been previously reviewed by Maga (1992). Thiazoles have a meaty flavor and are used extensively in producing meat flavorings. Thiazole, methyl thiazole and acetyl thiazole were tentatively identified in the extrudate. The mechanistic pathways for the production of thiazoles depend on thiamine decomposition during extrusion (Ho et al., 1989) or thermal degradation of cysteine (Shu et al., 1985; Zhang et al., 1988), however, 2-acetylthiazole, which may be formed from reaction of the Strecker aldehvde of cysteine with pyruvaldehyde (Mulders, 1973). In agreement with Bredie et al. (1998 a & b), dimethyltrisulfide is the aliphatic sulfur-containing compound identified in the extrudate at this extrusion temperature. regardless to moisture content. This polysulfide has been reported in the extrudate of yeast extract (Izzo and Ho, 1991) and high - gluten wheat flour (Hwang et al., 1994a&b). The possible precursors for this polysulfide are hydrogen sulfide and methanethiol which is a degraded product from sulfur-containing amino acid (cysteine, methionine, S-methyl methionine) (Madruga and Mottram, 1998).

Only a few pyrroles have previously been identified in extruded cereals, mainly in maize (Nair *et al.*, 1994). 2-Acetylpyrroline and acetyl

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pyridines were reported before in both popcorn (Buttery et al., 1997) and extruded maize (Bredie et al., 1998 a & b), but in addition to these compounds, another four pyrroles were identified in the extrudate. It was suggested that, alkylpyrroles formed *via* a pyrolytic degradation of the amino acids alone, whereas acyl or aldehydic pyrroles required the presence of a sugar source (Mottram and Whitfield, 1995; Baltes and Bochmann, 1987; Shieberle, 1991) and Buttery et al., 997). Buttery and Ling, 1995 have shown that acetvl pyrroles and pyridines are all important to popcorn aroma, the main odor description used by a sensory panel evaluating 2-acetyl-1-pyrroline was "pop-corn".

Short-chain aldehydes, ketones and various dicarbonylic precursors increased by decomposition of carbohydrates *e.g.* acetic acid, methyl ester, while others may be formed as Strecker degradation of amino acids e.g. 3methyl butanal (Farouk et al., 2001). The content of butyrolactone substantially increased too, while maltol is produced by thermolysis of Amadori compounds (Yaylayan et al., 1992). The origin of most long – chain aliphatic aldehydes, alcohols as well as aliphatic hydrocarbons is the oxidative and / or thermal degradation of lipids (Grosch, 1982). Alkanals detected among the volatiles could not have much pronounced influence on the resulting flavor as they were high molecular - weight compounds (6 - 12 C-atoms). The Maillard reactants had various effects on the products of lipid oxidation; the greatest one was on amounts

Tuste (2)/ Color parameters of extraued maile nour						
Sample	L*	a*	b*	h*	c*	ΔΕ
White blank	50.68	-9.26	9.21	135.68	12.72	
Black blank	50.86	1.6	25.94	84.42	28.03	
Extruded maize flour	50.46	15.68	76.16	78.58	77.73	71.44
Extruded marze nour	50.40	15.00	70.10	78.58	11.15	/1.44

 Table (2): Color parameters of extruded maize flour.

Table (3):	Sensory	evaluation	of extr	ruded	maize	flour.
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Property	Extruded maize flour
Intensity of browning	6.3
Pleasantness of odor	41.9
Intensity of odor	25.3
Texture (between fingers)	40.8
Ginger bread, roast, bread crust, roasted groundnuts	23.0
Burnt, caramel, bitter	14.1
Woody, peel, rubbery	12.0
After dough, flour, bread crumb	33.2
Spicy, sulphur, after onion, garlic	22.8
Penetrating, sharp, pungent	9.8
Fatty, oily, buttery	19.4
Earthy, musty, after earthy, mouldy, after sweet, wet dog	11.9
Malty, cocoa powder, sweet	25.0
Chemicals, synthetics, solvents	8.0
Others	

of aldehydes collected. Generally, the quantities of all aldehydes produced from lipids oxidation were reduced, saturated aldehydes were also reduced by a factor of two, while the unsaturated ones reduced by a factor of at least 10 (Farmer and Mottram, 1992). Aldehydes often have very low odor threshold values and can cause rancid odors in foods. Therefore, their reduction by the presence of Maillard reactants will be of some importance for the quality of foods (Bailey *et al.*, 1987). Also, it was suggested that, presence of amino groups somehow promotes the formation of 2-alkanones during heating (Farmer and Mottram, 1994).

Fatty acids, like long-chain alkanals, were also not substantial as flavor carriers. Hydrocarbons with 10 - 16 carbon atoms were present, but they can not be considered as substances of major importance because of their higher detection threshold (Farouk *et al.*, 2001). According to Ho *et al.* (1989), oxidative or thermal degradation of carotenoids leads to alkyl benzenes or terpenic derivatives, while phenolic acids degradation gives phenols.

Table (2) shows an evaluation for the browning degree in the extrudate. The increase of a\* and b\* corresponds to the increase in redness and yellowness, respectively, which occurs in the beginning of nonenzymatic browning. Products with more intensive green and blue color notes are formed only later, as a result of secondary reactions. Such reactions can not occur in course of very short extrusion time of 30 seconds and at relatively low temperature 120°C (Pokorny *et al.*, 2002).

Sensory evaluation of the extrudate is represented in Table (3). In agreement with the volatiles detected, many aroma properties could be presented by different compounds, e.g. malty (3-methylbutanal), sweet (furans and pyrans), cocoa (2-isopropyl-5-methyl-hex2-enal), bread crumb (pyrroles). and onion like (dimethyltrisulfide).This is generally in agreement with Bredie et al. (1998 a & b), in spite of the different technique used.

#### Conclusions

From the above results it could be concluded that the nonenzymatic browning was only moderate which is clearly observed through the color parameters of the extruded maize flour, however, using SPME extraction technique for the first time in this study and GC/MS, successfully extracted and identified more than 90 compounds, many of them were not reported before. The study was performed, also for the first time, at the standard industrial conditions including temperature and normal moisture content. Sensory evaluation of the extruded sample could be easily understandable in comparison to the identified compounds and their sensory properties.

#### **4. REFERENCES**

- Bailey M. E., Shin-Lee S. Y., Dupuy H. P., St. Angelo A. J. and Vercellotti J. R. (1987).
  Inhibition of warmed – over flavor by Maillard reaction products. In Wormed – over flavor of meat, St. Angelo, A. J. and Bailey, M. E., Ed., Academic Press, London. 237-266.
- Baltes W. and Bochmann G. (1987). Model reactions on roast aroma formation. III. Z. Lebensm. Unters. Forsch. 184: 478-484.
- Bredie W. L. P., Mottram D. S. and Guy R. C. E. (1998a). Aroma volatiles generated during extrusion cooking of maize flour. J. Agric. Food Chem. 46: 1479-1487.
- Bredie W. L. P., Mottram D. S., Hassell G. M. and Guy R. C. E. (1998b). Sensory characterization of the aromas generated in extruded maize and wheat flour. J. Cereal Sci. 28: 97-106.
- Buttery R. G. and Ling L. C. (1995). Volatile flavor components of corn tortillas and related products. J. Agric. Food Chem. 43: 1878-1882.
- Buttery R. G., Ling L. C. and Stern D. J. (1997). Studies on popcorn aroma and flavor volatiles. J. Agric. Food Chem. 45: 837-843.
- Camire M. E. (1998). Chemical changes during extrusion cooking. In Process – Induced Chemical Changes in Food; Shahidi, *et. al.*, Ed., Plenum Press, New York. 109-121.
- Chen J., Serafin F. L., Pandya R. N. and Daun H.(1991). Effects of extrusion conditions on sensory properties of corn meal extrudates. J. Food Sci. 56: 84-89.
- Farmer L. J. and Mottram D. S. (1992). Effect of cysteine and ribose on the volatile thermal degradation products of a triglyceride and three phospholipids. J. Sci. Food Agric. 60: 489-497.
- Farmer L. J. and Mottram D. S. (1994). Lipid Maillard interactions in the formation of volatile aroma compounds. In Trends in Flavor Research; Maarse H. and van der Heij, D. G., Ed., Elsevier Sci. B. V., Netherlands. 313-326.
- Farmer L. J., Mottram D. S. and Whitfield F. B. (1989). Volatile compounds produced in Maillard reactions involving cysteine,

ribose and phospholipids. J. Sci. Food Agric. 49: 347-368.

- Farouk M. A, Pudil F., Janda V. and Pokorny J., (2000). Effect of amino acids on the composition and properties of extruded mixtures of wheat flour and glucose. Nahrung. 44: 188-192.
- Farouk M. A, Pudil F., Janda V. and Pokorny J. (2001). Changes during the extrusion of semolina in mixture with sugars. Czech J. Food Sci.19: 24-30.
- Fors S. (1983). Sensory properties of volatile Maillard reaction products and related compounds: A literature review. In Maillard reaction in Foods and Nutrition; Walker, G. R. and Feather, M. S., Ed., ACS, Washington, D. C. 185-286.
- Fors S. M. and Eriksson C. E.(1986). Pyrazines in extruded malt. J. Sci. Food Agric. 37: 991-1000.
- Grosch W. (1982). Lipid degradation products and flavour. In Food Flavors, Morton, I. D. and MacLeod, A. J., Ed., Elsevier, Amsterdam. 325-398.
- Guth H. and Grosch W. (1993). Aroma compounds from extruded oat flour, changes during storage. Z. Lebensm. Unters. Forsch. 196: 22-28.
- Ho C.T., Bruechert L. J., Kuo M. C. and Izzo M. T. (1989). Formation of volatile compounds from extruded corn – based model systems. In Thermal Genration of Aromas, Parliament T. H., McGorrin, R. J. and Ho, C.-T., Ed., ACS, Washington, D. C. 504-511.
- Huber G. R. (1991). Carbohydrates in extrusion processing. Food Technol. 45: 160-161.
- Hwang H. I., Hartman T. G., Karwe M. V., Izzo H.V. and Ho C. T. (1994b). Aroma generation in extruded and heated wheat flour. In Lipids in Food Flavors, Ho, C.-T. and Hartman, T. G., Ed., ACS, Washington, D. C. 144-157.
- Hwang H. I., Hartman T. G., Rosen R. T., Lech J. and Ho C. T. (1994a). Formation of pyrazines from the Maillard reaction of glucose and lysine. J. Agric. Food Chem. 42: 1000-1004.
- Izzo H. V. and Ho C. T. (1991). Isolation and identification of the volatile components of an extruded autolyzed yeast extract. J. Agric. Food Chem. 39: 2245-2248.
- Madruga M. S. and Mottram D. S. (1998). The effect of pH on the formation of volatile compounds produced by heating a model system containing 5-Imp and cysteine. J. Braz. Chem. Soc. 9: 261-271.

- Maga J. A. (1992). Pyrazine update. Food Rev. Int. 8: 479-558.
- Maga J. A. and Sizer C. E. (1979). Pyrazine formation during the extrusion of potato flakes. Lebensm. Wiss. Technol. 12: 15-16.
- Mottram D. S. and Whitfield F. B. (1995). Volatile compounds from the reaction of cysteine, ribose, and phospholipids in low moisture system. J. Agric. Food Chem. 43: 984-988.
- Mulders E. J. (1973). Volatile compounds from the non – enzymic browning reaction of the cysteine / cystine – ribose system. Z. Lebensm. Unters. Forsch. 152: 193-201.
- Nair M., Shi Z., Karwe M. V., Ho C.-T. and Daun H. (1994). Collection and characterization of volatile compounds released at the die during twin screw extrusion of corn meal. In Thermally Generated Flavors; Parliament T. H, Morello, M. J. and McGorrin, R. J., Ed., ACS, Washington, D. C. 334-347.
- Pawliszyn J. (1997). In SPME, Theory and Practice, Wiley VCH, New York.
- Pokorny J., Farouk M. A., Pudil F. and Janda V. (2002). Effect of defatted soybean flour on the flavour of extruded mixtures with wheat flour. Czech J. Food Sci. 20: 229-236.
- Politz M. L., Timpa J.D. and Wasserman B. P.(1994). Quantitative measurement of extrusion–induced starch fragmentation products in maize flour using nonaqueous automated gel– permeation chromatography. Cereal Chem. 71: 532-536.
- Riha W. E. and Ho C. T. (1998). Flavor generation during extrusion cooking. In Process – Induced Chemical Changes in Food, Shahidi, *et al.*,Ed., Plenum Press, New York. 297-306.
- Schieberle P. (1991). Primary odorants of popcorn. J. Agric. Food Chem. 39: 1141-1144.
- Shibamoto T. (1977). Formation of sulfur- and nitrogen – containing compounds from the reaction of furfural with hydrogen sulfide and ammonia. J. Agric. Food Chem. 25: 206-208.
- Shibamoto T. (1980). Heterocyclic compounds found in cooked meats.J. Agric. Food Chem. 28: 237-243.
- Shu C. K., Hagedorn M. L., Mookherjee B. D. and Ho C. T. (1985). Volatile components of the thermal degradation of cysteine in water. J. Agric. Food Chem. 33: 438-442.

- Sizer C. E., Maga J. A. and Lorenz K. (1975). The occurrence of pyrazines in white bread crust and crumb. Lebensm.- Wiss. Technol. 8: 267-269.
- Yaylayan V. A., Fichtali J. and van de Voort F. R.(1992).Production of Maillard reaction flavour precursors by extrusion processing. Food Res. Int. 25: 175-180.
- Zhang J.(1994). Chemistry and protein deamidation: reaction kinetics, parameter effects and impact on flavor generation. Dissert. Abstr. Int. B., 54, 5457.
- Zhang Y., Chien M. and Ho C.-T. (1988). Comparison of the volatile compounds obtained from thermal degradation of cysteine and glutathione in water. J. Agric. Food Chem. 36: 992-996.

### تحليل المركبات الطيارة الناتجة عن بثق دقيق الذرة باستخدام جهاز الإستخلاص الدقيق ذو المادة الجاذبة الصلبة(SPME)

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#### ملخص

تم استخلاص المركبات الناتجة عن بثق دقيق الذرة عند حوالى 140 درجة مئوية و ذلك بواسطة جهاز الإستخلاص الدقيق ذو المادة الجاذبة الصلبة والتعرف عليها باستخدام جهاز كروماتوجرافيا الغاز – طيف الكتلة. وقد تم فصل أكثر من 90 مركباً بنجاح ، شكلت البير ازينات الجانب الأكبر منها تليها الفيور انات وتم التعرف أيضا على بعض البيرولات إلى جانب بعض المركبات الكبريتيه. وعلى الرغم من ضألة تركيز بعض هذه المركبات وذلك نتيجة لدرجة الحرارة المنخفضه للبثق، إلا ان معظم هذه المركبات لها خواص حسية من حيث الطعم والرائحه تؤثر فى المنتج النهائي. وعلى النقيض فإن الألديهيدات والأحماض الدهنية، والكيتونات، والهيدروكربونات، والتى تم أيضا التعرف عليها لها تأثير أقل حسيا على المنتج النهائي. والحدير بالذكر أن معظم هذه المركبات ناتجه عن تفاعلين رئيسيين هما تفاعل مها تأثير أقل حسيا على المنتج ونتيجة لعدم شدة تفاعل ميلارد فإن التغير اللونى الناتج عن البثق يرى من خلاله المراحلة، وكذلك نتيجة لما تؤليل قل ونتيجة لعدم شدة تفاعل ميلارد فإن التغير اللونى الناتج عن المتق المركبات الكرماة، وكذلك نتيجة لدرجة المركبات الم

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