INVESTIGATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS AND STRATEGIES OF THEIR DECREASE IN SMOKED MEAT PRODUCTS

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Abstract – This paper analyzes the relationship between the quantitative content of PAHs in smoked meat products and product composition, packaging material and smoking technology. The indicators of PAHs presence have been revealed, the potential ways of PAHs reduction are presented.

Key Words – polycyclic aromatic hydrocarbons (PAHs), phenols, smoked meat products

I. INTRODUCTION

Smoke fume is generated during wood pyrolysis. The basis for pyrolysis is the free radical reactions of thermodestruction of hemicellulose, cellulose and lignin, taking place at a temperature higher than 200°C. The constitutive parts of wood, about 50% cellulose, almost 25% lignin and about 25% hemicelluloses (not counting the water), are turned therewith to phenols, alcohols and carbonyl compounds.

The positive effects of the penetration of the smoke substances into a product and the physico-chemical transformations in it are the development of taste and odor of a smoked product, and the preservative action (bactericidal, antioxidative and antiproteolytic effects). However, smoking of food products is accompanied by the development of the toxicologically harmful smoke components, namely, polycyclic aromatic hydrocarbons (PAHs) [1].

PAHs have pronounced carcinogenic, mutagenic and teratogenic effects on humans. The problem of PAHs is especially acute because they have the ability of bioaccumulation and it is impossible to set up the limits for them, below which these substances would not possess the carcinogenic potential [2].

EC countries have been toughening up the norms of PAHs content; the list of controlled substances has been expanded. Since September 2012, along with already established maximum allowed content of benzo[*a*]pyrene (5 μg/kg), four PAHs (benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene and chrysene) have been obligatory controlled, the summary content of which should not exceed 30 μg/kg. From September 2014, the norm for benzo[*a*]pyrene is not more than 2 μg/kg, for 4 PAHs not more than 12 μg/kg [3].

The high carcinogenic activity of minor PAHs, their chemical stability and the synergetic effect of the several PAHs exposure confirm the necessity of their tough control in meat products.

II. MATERIALS AND METHODS

Analysis of PAHs was performed by high performance liquid chromatography (UPLC) on the chromatograph Ultimate 3000 (Dionex) with fluorescent detector RF200 (Dionex) and the column Supelco LC-PAH 150x4.6 mm, 5 μm. The used chromatographic column is able to separate the structural isomers of PAHs due to the silica gel particles chemically modified with phenyl groups. The high sensitivity of fluorescent detector to PAHs allow to detect even the trace amounts at the level of 1 ppb. Use of solid phase extraction on silica gel (Silica – SPE Bulk Sorbent, Agilent) allow to clean samples from foreign organic impurities.

Analysis of alcohols, carboxylic acids, esters and phenols was carried out using a gas chromatograph 7890A (Agilent Technologies) coupled with a mass-spectrometric detector 5975C VL MSD (Agilent Technologies).

III. RESULTS AND DISCUSSION

Earlier studies showed that the main role in the specificity of the flavor play phenolic and carbonyl substances as well as *β*-lactons. The key compounds in the smoke fume aroma are the following: cyclotene, veratrole, p-ethylphenol,

guaiacol, 4-methylguaiacol, 4-propylguaiacol, methylsyringol [1]. Besides the above mentioned substances, the research that we conducted by gas chromato-mass spectrometry allow us to detect in high quantities terpene alcohols (phytol, iso-phytol and others) in the amount of 0.01-0.1%, carboxylic acids (phthalic acid and others) in the amount of 0.01-0.05%; phenolic substances (phenol, diphenylmethane, 3,3'-dimethylbipheny-l,2,2',3,3'-tetramethylbiphenyl and others) in the amount of 0.05-0.2%; and esters (dibutyl phthalate) in the amount of 0.1-0.3%, which create the flavor of a product, as well as toxic substances such as aromatic amines (aniline) in the amount of 0.01-0.05%, acyclic hydrocarbons (heneicosane) in the amount of 0.02-0.1%, aromatic hydrocarbons (naphthalene) in the amount of 0.02-0.05% and carcinogenic polycyclic aromatic hydrocarbons in the amount of 5-50 µg/kg.

It is estimated that the share of phenols in the formation of the typical smoking aroma on the average is 66%, the share of the carbonyl substances is 14% and of the other constituents is 14% and 20%, respectively. The investigations of the treatment of the fatback samples with phenols isolated from liquid smoking preparations showed that as phenolic substances dissolve into a fat fraction of fatback consisted mainly of saturated triglycerides, on the average, about 75% of the phenolic substances of the preparation were not identified later on.

Today, the hypothesis about the neutrality of fats relative to the smoking components is not refuted.

For the time being, only the involvement of protein and carbohydrate constituents in the reactions of chemical interaction with the smoking substances has been indisputably proven [1]. On the basis of the analysis of the PAHs quantitative content, however, it was shown that in raw smoked sausages with backfat in their composition, the PAHs residual quantity is up to 30% higher than in the products of this type of smoking, which composition did not include backfat. The tendency toward the carcinogenic PAHs accumulation precisely in the fat fraction of a product is evident.

It was interesting to assess the influence of the conditions of the formation of the smoke components generated as a result of wood decomposition on the PAHs quantitative content in smoked meat products. According to the results of the study a higher temperature of smoke formation resulted in the increase in the PAHs concentration in a product. The increase in temperature led to the increased CO and CO_2 content and the reduction of the oxygen concentration. The PAHs quantitative content grew in direct proportion as the smoke generation temperature and the CO and CO_2 concentrations were increasing and in inverse proportion to the oxygen concentration.

Figure 1 demonstrates the growth in the 15 PAHs concentration and separately benzo[*a*]pyrene depending on the increase in a temperature of smoke generation.

Table 1. Content of the 15 PAHs in smoked pork depending on a temperature of smoke formation

Name	Toxic equivalence factor [4]	Toxic equivalence factor [5]	PAHs content, µg/kg		
			250°C	450 °C	650 °C
Cyclopenta[*c,d*]pyrene	–	–	1.19	1.6	1.98
Benzo[*a*]anthracene	0.1	0.145	1.75	2.50	3.11
Chrysene	0.01	0.0044	1.83	2.50	3.40
5-methyl chrysene	–	–	0.13	0.15	0.26
Benzo[*j*]fluoranthene	0.1	0.12	0.04	0.05	0.13
Benzo[*b*]fluoranthene	0.1	0.12	0.48	0.60	1.03
Benzo[*k*]fluoranthene	0.1	0.052	0.12	0.14	0.22
Benzo[*a*]pyrene	1.0	1.0	0.47	0.59	0.76
Dibenzo[*a,l*]pyrene	–	–	0.02	0.03	0.10
Dibenzo[*a,h*]anthracene	1.0	1.11	0.12	0.18	0.26
Benzo[*ghi*]perylene	0.01	0.021	0.44	0.62	0.99
Indene[1,2,3-*cd*]pyrene	0.1	0.278	0.38	0.50	0.75
Dibenzo[*a,e*]pyrene	–	–	0.36	0.50	0.69
Dibenzo[*a,i*]pyrene	–	–	0.04	0.05	0.14
Dibenzo[*a,h*]pyrene	–	–	0.07	0.10	0.19
% Benzo[*a*]pyrene of the total amount of PAHs			6.32	5.83	4.71

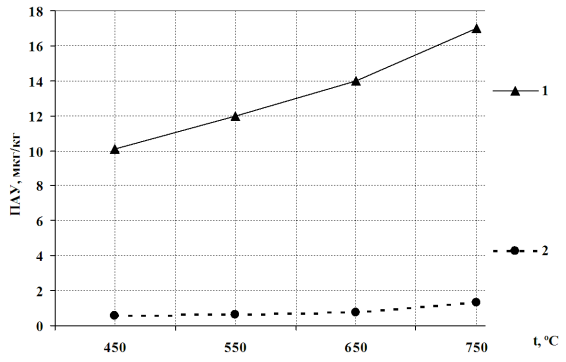

Figure 1 The relationship between the temperature of the generation of beech wood smoke and the 15 PAHs (1) and benzo[*a*]pyrene (2) content

Analyzing the obtained data regarding the packaging material, it was found that in the fume smoked meat products without casing the summary 15 PAHs content was 25% higher than in products produced in natural (little gut, bung) and artificial (protein and fibrouse) casings independent of the type of smoking. The least permeable for carcinogenic substances was the fibrouse casing. The duration of smoking also influenced the PAHs quantitative content. Thus, in raw smoked meat products in a natural casing the PAHs content was 30% higher than in semi-smoked sausages also produced in a natural casing.

Analysis of the PAHs quantitative content in meat produce in a framework of the certification showed that 8 PAHs namely benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene, chrysene, dibenzo[*a,h*]anthracene, indene[1,2,3-cd]pyrene were most frequently detected.

The summary percent content of 8 above listed PAHs was on the average more than 75% of total PAHs amount. Another factor in favor of the selection of the 8 above listed PAHs as an indicator of PAHs presence is the high degree of recovery, which is varied from 79.2 to 91.4%, whereas for dibenzo[*a,l*]pyrene, dibenzo[*a,e*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*a,h*]pyrene the degree of recovery was 48.2 to 64.2%.

The next step of the research was the search for the possible ways of the carcinogenic burden reduction when consuming smoked products. The development of the modern technologies of cleaning of volatiles emissions and sewage allowed to achieve multiple reduction of PAHs by photo-oxidation and microbial utilization.

However, it is not possible to use these technologies for food products.

Table 2. The protective effect of PAHs penetration from the vapor-gas phase into the product during thermolysis of beech wood

Name	PAHs concentration in a product, μg/kg			
	1 control	2 paper	3 ascorbic acid	4 acetic acid
Cyclopenta[*c,d*]pyrene	2.76	0.21	1.28	0.39
Benzo[*a*]anthracene	2.08	0.42	0.73	0.23
Chrysene	2.18	0.56	0.79	0.31
5-methyl chrysene	1.79	0.32	0.67	0.30
Benzo[*j*]fluoranthene	0.10	0.03	0.05	0.01
Benzo[*b*]fluoranthene	1.08	0.31	0.48	0.14
Benzo[*k*]fluoranthene	0.31	0.06	0.11	0.03
Benzo[*a*]pyrene	0.82	0.20	0.29	0.08
Dibenzo[*a,l*]pyrene	0.11	0.006	0.015	0.005
Dibenzo[*a,h*]anthracene	0.31	0.13	0.04	0.02
Benzo[*g,h,i*]perylene	2.22	0.76	0.95	0.26
Indene[1,2,3-cd]pyrene	0.83	0.28	0.37	0.07
Dibenzo[*a,e*]pyrene	0.97	0.26	0.33	0.17
Dibenzo[*a,i*]pyrene	0.11	0	0	0
Dibenzo[*a,h*]pyrene	0.11	0	0	0
Σ	15.78	3.55	6.11	2.02

One of the possible ways to reduce the PAHs quantitative content can be the use of hurdle technologies. By hurdle technology is implied a film, membrane protection or a composite casing preventing or significantly reducing PAHs diffusion from a gas-air medium into a product.

The thermal decomposition of wood was performed by heating wood sawdust of different species at 200-700^{o}C with the following treatment of a food product with the obtained smoke fraction during 6 hours at a temperature of the processing product heating of 35-50^{o}C.

The natural casing according to SN 32/34 EBP, protein casing from collagen of splits of cattle hides and fibrouse casing on a paper basis with a natural cellulose coating of the casing according to GOST 16131-86, writing paper with density of 80 g/m^2, on which surface a 20% fat containing micro/nanoemulsion of vegetable oil or animal fat was applied, were used as protective films. Additionally, a product was hold beforehand in the 9% solution of acetic acid or 3% solution of ascorbic acid for 24 h in order to protect the processing food material from smoke components.

IV. CONCLUSION

On the basis of the research results, it can be concluded that it is possible to achieve the PAHs content reduction in several ways. One of them is the reduction of fat content in the formulation of smoked products. With that, the PAHs content reduction is not associated with the reduction of phenolic substances, which are responsible for taste and aroma of smoked products. The main parameter influencing the PAHs generation is the temperature of the smoke generation.

The advantages of use of protein and, especially, fibrouse casings compared to natural casings are evident from the obtained data. Protein and fibrouse casings are denser, their protein-cellulose base is not highly fat swelling, but the PAHs penetrability through such barriers is in many respects hampered.

The performed preliminary investigations showed that a number of ingredients assist the production of smoked meat products with reduced PAHs content. These ingredients include many kinds of spices, ascorbic acid and a variety of natural stabilizers. The obtained data regarding the 15 PAHs quantitative content allow to reveal the indicators of PAHs presence, which are 8 above listed PAHs.

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