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SOLVING THE PROBLEM OF CONTAMINATING SMOKED FOOD WITH CARCINOGENIC COMPOUNDS OF SMOKE

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ABSTRACT

Meat and fish smoked products, widely produced nowadays, occupy a permanent place in the mass diet. The consumption of smoked meat is estimated by FAO at 15.6 million tons in 2019 (+40 % growth over the past ten years). This is due to the increased incomes of consumers in many countries, which made meat and fish smoked products, once classified as "premium" delicacies, more accessible to the majority. There has been a shortage of high-quality raw materials, which, combined with a highly competitive food market, forces manufacturers to reduce their costs by using non-traditional raw materials. The latter leads to increased use of processing raw materials with smoke to effectively mask individual defects in taste, appearance and consistency of products. As a result, there is a carcinogenic contamination problem because of polyaromatic hydrocarbons (PAHs) presented in the smoke and smoking liquids, and the growth of cancer. PAHs are formed as a result of pyrolysis of wood during smoke generation at temperatures above 450-480 °C. Currently used smoke generators and schemes for cleaning smoke from PAHs are not effective enough, so they do not eliminate the main cause of PAH formation, uncontrolled pyrolysis. The principal solution to the problem is to develop methods and equipment for producing smoke at temperatures below carcinogenic peaks. A successful solution is the method for producing smoke with an infrared power supply, implemented in the design of IR smoke generator (IR-SG). The device allows to reliably maintain the pyrolysis temperature of wood below 450 °C. The effectiveness of the method and apparatus is confirmed by studies of products smoked with IR-SG, in which the content of Benzo(a)pyrene is less than 0.0002 mcg/kg, which is lower than the maximum permissible concentrations of this compound in food.

Keywords: *Smoked products, carcinogenic compounds, smoke generation, infrared smoke generator.*

INTRODUCTION

Smoking is the oldest method of processing meat and fish, which gave the opportunity to improve the taste of the food and preserve it reliably and for a long time. Meat and fish smoked products rich in protein are produced today in a wide range and different prices, so they occupy a permanent place in the diet of modern people. The consumption of smoked meat is estimated by the FAO in 2019 at 15.6 million tons, with an increase of 40% over the past ten years. The smoked meat industry today is highly fragmented, with producers located in North America with a share of 32.92% of global production, and in Europe. The world leader in the production of smoked food is WH Group, with a global market share of 10.18% in 2015 (IndustryResearch, 2020).

The preserving factors during smoking are dehydration of the product to a residual mass fraction of water no more than 40% of the total weight (cold smoking method) and high temperature from 60 to 120 °C (hot smoking method). In both methods, the raw materials are also affected by chemical preservatives in the smoke – phenols and carbonyl compounds. Phenols act as powerful antioxidants and antiseptics, to a lesser extent, forming organoleptic signs of smoking, while carbonyl compounds are mainly responsible for the formation of taste, aroma and color of the smoked meat and have a weak bactericidal effect. In total, the smoke contains more than 10,000 organic compounds which are products of incomplete combustion of wood components such as cellulose, hemicellulose and lignin, including acids, alcohols, and esters. (Kurko, 1960).

The absolute negative effect of smoking is the contamination of products with pro-carcinogenic and carcinogenic compounds – polyaromatic hydrocarbons (PAHs) of the 3,4-Benz(a)pyrene type, as well as nitrosamines (NA). PAHs are formed as a result of pyrolysis of wood during the smoke generation at temperatures above 450-480°C (Kim, 2004).

Despite the high level of carcinogenic hazard (Rozentale *et al*., 2018), the enhanced taste of smoked products makes them a common and affordable delicacy these days. The shortage of high-quality raw materials, combined with a highly competitive food market, forces manufacturers to reduce their costs by using non-traditional raw materials, or the materials with reduced commodity characteristics. The latter leads to an increasing use of Smoking to effectively mask certain defects in taste, appearance and consistency of products. Increased consumer incomes in many countries have made meat and fish smoked products, in the recent past classified as premium delicacies, more accessible. This is confirmed by the steady growth in the consumption of smoked products, shown in the diagram in figure 1 (FAO, 2018).

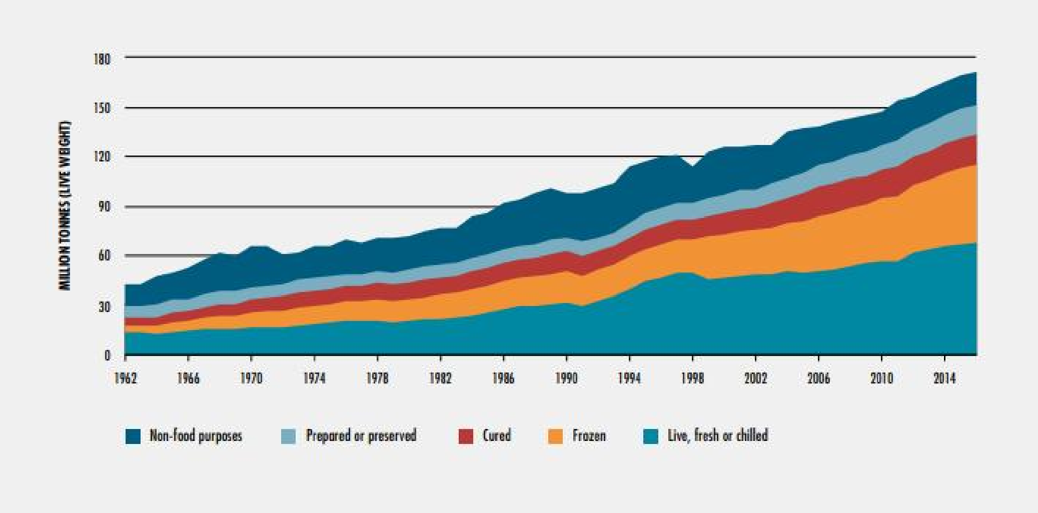

Figure 1. Utilization of world fisheries production, 1962–2016

The global smoked meat market is estimated at $34,660 million in 2020 and is expected to reach $39,330 million by the end of 2026, increasing by an average of 1.8% during 2021-2026. The main regions of consumption of meat and fish smoked products today are North America, Europe, China and Japan (IndustryResearch, 2020).

As a result, there is a problem of contamination of mass-consumption food with carcinogens (PAHs) in the composition of smoke or smoking liquids and a potential significant increase in cancer diseases. Currently used smoke generators and schemes for cleaning smoke from PAHs are not effective enough, so they do not eliminate the main cause of PAH formation – uncontrolled pyrolysis (Shokin *et al*., 2020).

The objective of the present paper is to provide an overview of the effective solution of this problem with a special focus on the development of new methods of smoke generation and smoke generators, which reliably maintain the pyrolysis temperature below carcinogenic peaks.

MATERIAL AND METHODS

The article is based on an extended review of secondary and primary data collected from the scientific and technical publications and patent search, as well as during experiments conducted in the winter of 2019-2020 at the research laboratory of the Department of Food Production Technologies of Murmansk State Technical University and at the University's educational and experimental workshop. In the process of IR smoke generation, the distribution of temperature and moisture content in the fuel layer (sawdust of deciduous trees with bulk density from 84 to 154 kg/m^3 with an initial humidity of 45 to 60 %), for which the temperature T (K) and relative humidity U (% или kg/m^3) were measured at various points of layer with a coordinate x (m). The layer had a constant irradiated surface area S (m^2) in all experiments, which was provided by the design features of the IR smoke generator. The coordinate x characterizes the position of the measurement point in the height of the layer as the distance from the irradiated surface, measured by the normal passing through the measurement point deep into the layer. The thickness of the layer corresponds to the distance measured by the normal between the plane of the irradiated surface of the sawdust layer and the plane of the sawdust layer farthest from it (it varied from 0.005 m to 0.12 m). In all experiments, free filling of sawdust (without pressing) is used, which forms a layer of fuel of the final thickness as a porous layer containing solid wood particles, moisture condensate and moist air with a high content of water vapor. To determine the moisture content of sawdust, a standard weight method was used – a sample of sawdust weighing from 1 to 3 g, taken point-by-point directly from the sawdust layer at the measurement point, was dried in a drying chamber at 105 °C to a constant mass. The temperature of the fuel layer was determined using calibrated needle thermocouples with measuring ranges from minus 50 to 1200 °C (measurement accuracy (±0.1 °C)) placed directly at the measurement point. All experiments were performed at least three times over. Mathematical processing of the experiment results was carried out using generally accepted methods of mathematical statistics. Measurements of fuel temperature and humidity were performed both before and during smoke generation. The technical capability of measurements directly in the process of smoke generation was provided by the design features of the pilot model. Temperature measurement of the pyrolysis of wood during the IR smoke generation was performed according to the developed original method (Shokina et al., 2019), which provides for production of model of wood specimen geometry which corresponds to the porous structure of the layer of sawdust a given bulk density. For correct measurements, the model sample had an initial humidity corresponding to that of the sawdust layer. A needle-shaped thermocouple was placed in the model sample, for which it was technically possible to take readings continuously during the entire process of thermal decomposition of the model sample under the influence of IR radiation in the smoke generator. The carcinogenic safety of smoke from an IR smoke generator was determined indirectly based on the results of determining the mass fraction of 3,4-Benz(a)pyrene in smoked fish fillets made according to the traditional scheme of cold smoking. For the study, a standard method was used based on the extraction of Benz(a)pyrene by hexane from a product pretreated with an alcoholic solution of caustic potassium, the separation of a fraction of polycyclic hydrocarbons by thin-layer chromatography on aluminum oxide, and the quantitative determination of the resulting fraction of Benz(a)pyrene by low-temperature spectrofluorometry. The range of determined values of the mass fraction of Benz(a)pyrene in the analyzed products by this method is from 0.0002 to 0.005 mg/kg.

RESULTS AND DISCUSSION

The analysis of Russian smoke generator designs has shown the predominance of endothermic devices with internal heat generation (more than 70% of the total number of operated devices and devices presented on the smoking equipment market). Wood fuel is heated in these devices by partial inflaming. Endothermic smoke generators are characterized by frequent fuel firing, uncontrolled temperature growth in local areas up to 800-1200°C, and, as a result, by high contamination of PAH smoke. Analysis of exothermic smoke generators (with external heat generation) showed common technical characteristics: a simple design, a primitive system of water extinguishing of open flames, the absence of any mechanization of the process, the absence of automatic monitoring and control. In general, most of the devices for producing smoke of both types can be characterized as obsolete (Shokin *et al*., 2020).

Imported exothermic smoke generators, currently available on the Russian market, are more competitive than domestic ones due to numerous options that allow to:

- prevent the occurrence of hot spots of fuel overheating during the smoke generation process;
- monitor and control (automatically) important technological parameters of smoke-relative humidity, temperature, air-weight concentration;
- reduce energy and wood fuel consumption per unit of finished product;
- effectively clean up smoke emissions into the atmosphere.

The most widely used in Russian meat and fish enterprises are smoke generators of the SUPER SMOKE type by VERINOX, chip smoke generators by AUTOTERM, smoke generators by REICH and VEMAG that differ slightly in design (Shokin *et al*., 2020).

The advantage of foreign manufacturers of smoke generators is to offer consumers, as a rule, a whole product line of devices. This provides consumers with a wide range of equipment designs, depending on the purpose of processing food raw materials and capabilities. For example, there are product lines of smoke generators from German and Polish companies "FESSMAN", "Schröter" or "FEMAG", in which the choice is given between a smoldering smoke generator (RATIO-TOP), a friction smoke generator (RATIO-FRICTION) and a liquid one (RATIO-LIQUID). The disadvantage inherent in most foreign and Russian smoke generators up to date is the lack of automatic control of the temperature of wood pyrolysis, which leads to a high risk of spoiling the smoke with PAH.

The Department of Food Production Technologies of Murmansk State Technical University has developed a method for producing smoke using infrared energy supply to wood material (Shokin *et al*., 2020).

In thee IR smoke generator, a layer of wood sawdust with a moisture content of 45 to 60% and a bulk density of 104 to 154 kg/m^3 is irradiated with infrared rays (the radiation wavelength ranges from 3.5 to 5.5 microns, the distance from the fuel surface to the wood is from 0.08 to 0.10 m). The amount of energy supplied to the sawdust layer is consistent with the kinetics of wood heating.

As it was found, the kinetics of heating the fuel layer is mainly affected by the bulk density of sawdust and their moisture content. These parameters affect the absorption, transmission, and reflectivity of the fuel layer, which determine the amount of absorbed radiant energy. Controlling the moisture content of the fuel directly during the smoke generation process, as well as correctly accounting for its specific surface area, allows to reliably manage the pyrolysis temperature and maintain it in the desired range. This, in turn, minimizes the risk of PAH formation.
The main technical parameters of the IR smoke generator in comparison with other smoke generators, widely represented in meat and fish enterprises in Russia, are shown in table 1.
The data presented below shows that the IR SG has a number of competitive advantages over other SGs due to its ability to manage the process of producing smoke at a stable temperature, and guaranteed high carcinogenic safety of the resulting smoked products.

Table 1. Technical and economical characteristics of the IR smoke generator.

Feature	Content	Comparison with analogs
Pyrolysis temperature, °C	from 350 to 400	Operating modes guarantee stable temperature maintenance in the specified range throughout the pyrolysis process, unlike most other devices
Sawdust consumption, kg/m^3 of process smoke	no more than 4,5	Less on average by 50% compared to other devices
Electric power consumption, kW per hour	from 2,75 to 8, 25	Less with comparable performance by 40-100% compared to other devices
Performance, m^3 of smoke per hour	no less than 43,5	Comparable to the performance of other devices with lower fuel consumption
Productivity, tons of cold-smoked finished products per day	up to 1,0	-
Mass fraction of 3,4-Benz (a)pyrene, mcg per 1 kg of cold-smoked finished products	less than 0,0002	Significantly lower than the maximum permissible concentrations in Russia and the European Union

*Source: Author's elaboration based on the personally conducted experiments and on the review of scientific and technical publications and patent search.

The problem of computer simulation of the smoke generation process is also very relevant. The mathematical model can be used as the basis for automated calculation of the pyrolysis temperature, which is the main parameter that determines the carcinogenic safety of smoke.
On the basis of the known differential equations of heat and mass transfer and the experiments carried out, a description of the processes of mass and heat transfer during pyrolysis of fuel in a smoke generator with an IR power supply is proposed in the form of a system of differential equations (Shokin *et al*., 2020):

$$\begin{cases} C \cdot \circ \cdot \dfrac{\partial T}{\partial {}^{2}} = {}^{a} \cdot \dfrac{\partial^2 T}{\partial x^2} + r \cdot \sim \cdot \dfrac{\partial U}{\partial {}^{2}} + w(x) + q(x) \\ \dfrac{\partial U}{\partial {}^{2}} = D_u \cdot \dfrac{\partial^2 U}{\partial x^2} + D_t \cdot \dfrac{\partial^2 T}{\partial x^2} \end{cases}, \qquad (1)$$

where $C \cdot \circ = c_W \cdot \dfrac{U \cdot \circ_{SD}}{1-U} + c_{SD} \cdot \circ_{SD}$ – volume heat capacity of the water-sawdust mix, j/(m^3·K) ($c_{SD.}, c_W, \circ_{SD}$ – specific heat capacities of dry sawdust (*SD*) and water (*W*), j/(kg·K), and the density of sawdust, kg/m^3, the heat capacity of steam is neglected; U – humidity of sawdust, unit fractions);

T – temperature of sawdust, K;

² – duration, seconds;

ª – the coefficient of thermal conductivity of the wood sawdust layer, set by the specific surface of sawdust and its moisture content, W/(m·K);

r – latent heat of vaporization, j/kg;

~ – the coefficient that determines the percentage of participation of condensation and vaporization processes in the volume of the layer, unit fractions;

U – moisture content of sawdust, kg/m^3;

$w(x)$ – volumetric heat absorption in the sawdust layer with a coordinate x, that is counted from the lower border of the sawdust towards the IR emitter, W/m^3;

D_U – the coefficient of potential conductivity of moisture transfer, characterizes the transfer of moisture in the fuel layer due to capillary phenomena and moisture adsorption on the surface of sawdust, m^2/seconds;

D_t – the coefficient of thermal and water transfer potential conductivity in the sawdust layer, (kg/(K·m·seconds);

$q(x)$ – heat of thermal decomposition of wood in the volume of the layer, W/m^3.

It follows from the equations that the IR smoke generation process is a complex heat and mass transfer process. Pyrolysis of wood with the formation of smoke occurs in a thin (thickness from 1 to 3 mm) surface layer of fuel, which directly absorbs infrared radiation. This process is a phase transition and is accompanied by the release of heat, which forms its internal source in the fuel layer. Moisture and heat move in the sawdust layer by several mechanisms simultaneously. The radiant stream, partially absorbed by a thin surface layer of wood fuel (with a moisture content of 40 to 55%), forms a large temperature gradient. Under the influence of this gradient, heat moves deeper into the layer by the mechanism of thermal conductivity. Under the influence of the difference in moisture content of the lower layer and the dry surface layer, moisture moves in the layer by the mechanism of moisture conductivity. The third mechanism is the convection moisture exchange in the air layers presented in the sawdust layer (formed by large voids between the particles). Moisture transfer in the fuel layer maintains a stable temperature of the smoke-generating layer.

Equation (1) is solved for the given boundary and initial conditions using a numerical method (the grid method, specifically). The values of thermal coefficients (coefficient of thermal conductivity, volumetric heat capacity), coefficients of the differential equation (potential conductivity of moisture transfer and heat transfer) are obtained by solving the inverse problem and calculating. The computer program is written for predicting the temperature at any point in the fuel layer at any time of smoke generation. When developing the program, the thickness of the elementary fuel layer in which pyrolysis occurs directly (from 1 to 3 mm) is taken into account.

When comparing the results of modeling the kinetics of fuel heating with experimental data (figure 2), a satisfactory convergence and an admissible error were found.

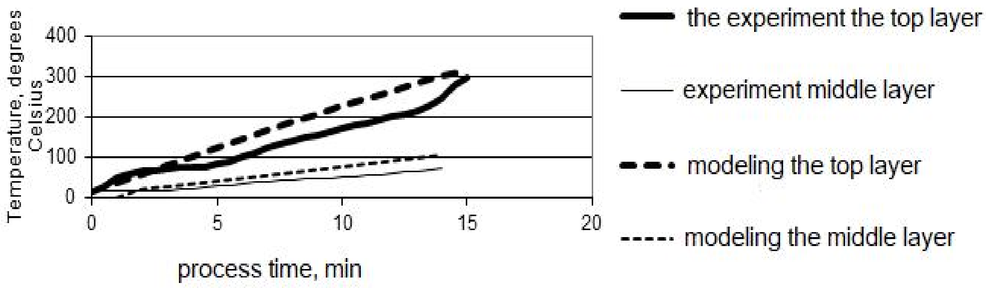

Figure 2. Fuel heating kinetic curves by layer thickness: bulk density of sawdust – 118 kg/m^3, moisture content of sawdust – 35%, the amount of moisture added in the process – 40% of the fuel mass

CONCLUSIONS

The consumption of smoked meat and fish is growing in the world, which is a potential threat to the growth of cancer diseases in the population of advanced and emerging countries. In the coming years, the problem of increasing the carcinogenic safety of smoked meat and fish will be extremely relevant. The most effective solution to the problem is to develop innovative methods of smoke generation and their hardware design.

An example of a successful solution to the problem is a smoke generator with an infrared power supply. The device design allows to reliably control the pyrolysis temperature of wood fuel (sawdust with a bulk density of 104 to 154 kg/m^3 and a moisture content of 40 to 60%) by supplying heat energy in an amount consistent with the kinetics of wood heating. A mathematical model of the IR smoke generation process has been developed, which is the basis of a computer program for predicting the temperature of fuel pyrolysis. The stability of the pyrolysis temperature in the IR smoke generator is confirmed by studies of the content of 3,4-Benz(a)pyrene in smoked mackerel fillets, made with the use of the IR-generated smoke.

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