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Review paper

ABOUT A «DIGITAL TWIN» OF A FOOD PRODUCT

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Key words: *digital twin, simulation model, chemical composition, functional-technological properties, food product*

Abstract

The paper presents definitions of digital twins. The authors examine a hypothesis that a digital twin of a food product is a mathematical (simulation) model that includes the whole variety of factors influencing quality and safety. An approach to the mathematical setting of the structural optimization task at different stages of description of the technology for a food product digital twin is analyzed. The first stage, which has several levels, is connected with correspondence of the nutritional and biological values to the medico-biological requirements. The second stage is linked with predetermination of structural forms, the third with perception of sensory characteristics (color, odor and so on). The universal method for assessment of quality and efficiency of a food product digital twin using the generalized function (integral index) is described. Different individual responses can be components of the additive integral index: physico-chemical, functional-technological and organoleptic.

Introduction

The term digital twin appeared in 2003 in the framework of the Course on Product Lifecycle Management (PLM) in Florida Institute of Technology (https://www.fit.edu/) [1].

Over the last decade, many definitions of a digital twin have appeared. The most widespread definitions are given in [2]:

1) A digital twin is an integrated multiphysics, multiscale, probabilistic simulation of an as-built vehicle or system, which uses the best available physical models, sensor updates, history and so on [3];
2) A joint model of a real machine, which works on the cloud platform and simulate the health condition with integrated knowledge both from manageable data of analytical algorithms and from other available physical knowledge [4];
3) A digital twin is a digital replication of a living or non-living physical entity. Combining physical and virtual worlds, data are transformed unnoticeably allowing a virtual entity to exist simultaneously with a physical entity [5];
4) The use of digital replication of a physical system for real-time optimization [6];
5) A dynamic virtual representation of a physical object or system throughout the life cycle using real-time data for understanding, learning and reasoning [7];
6) A digital twin is a real mapping of all components in the product life cycle using physical data, virtual data and data of their interaction [8].

A digital twin has been introduced in the KAMAZ sites. KAMAZ has already created the 3D models of 28 units of machine tools with CNC and 20 universal machine tools as well as more than 50 units of different technological equipment (robots, manipulators, turn-over devices, roller tables). The 3D models are used in simulation of mechanical processing and assembly as well as for arrangement of equipment in the 3D plant design.

Digital copies came into use for effective operation of trains Sapsan and Lastochka. Virtual models are used for optimization of rail transportation. Thereby, costs of repair work are reduced and operations that duplicate each other are eliminated. In 2018, introduction of a production digital twin was also announced by «Transmashholding». The system calculates the results of production plan fulfillment with given parameters in a matter of minutes and quickly reacts on the customer requests [9].

Definition No.4 is the most suitable for the term digital twin of a food product.

The present paper examines a possibility of using the theory of a digital twin in description of food products. The authors of the paper propose a hypothesis that a food product digital twin is a virtual model of a product, namely its mathematical model (simulation model*) that combines the whole variety of factors from the chemical composition and functional-technological properties to organoleptic indices. Using a digital twin of a food product before its launch into production, engineers-technologists can analyze the nutritional, biological and energy values as well as other product characteristics.

The dispersion of parameters and properties of biological raw materials can be compensated in the real-time operational conditions by selection of optimal strategies of component redistribution and alteration of technological schemes depending on the actual resource and component composition of biological raw materials. Therefore, each possible condition of the input flow of biological raw materials will be contrasted with a certain structural and regime alternative that ensure maximum product processing from a raw material unit at maximum approximation to the normative indices.

* A simulation model is a logical mathematical description of an object that can be used for computer experiments for design, analysis and assessment of object function [10].

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Main part

By a mathematical (simulation) model is meant an equation that links an optimization parameter with factors

$$y = \varphi(x_1, x_2 \ldots x_k),$$

where $\varphi(x_1, x_2 \ldots x_k)$ is a response function.

To design an experiment, a factor should have a certain number of discrete levels. A fixed set of factor levels determines one of possible states of the object under investigation. At the same time, this is a condition for conducting one of possible experiments. If we try all possible sets of states, we will have many different states of the object under investigation. The number of possible experiments is determined by the equation

$$N = p^k,$$

where, N — number of experiments; p — number of levels; k — number of factors.

The real objects usually have huge complexity. For example, a system with 5 factors at 5 levels that might appear at first glance to be simple has 3125 conditions ($N = 5^5 = 3125$), and for 10 factors at 4 levels their number will be above a million ($N = 4^{10} = 1048576$). In these cases, performance of all experiments is practically impossible. Therefore, advantages of using the digital twin technology become immediately evident.

Setting up the task of structural optimization at different levels of description of the digital twin technology for a food product is reduced to minimization of deviations of the actual parameters from the given normative (reference, desired) values with finding a balance regarding the chosen indices between the input and output material flows.

At the first stage of the balance analysis by raw materials for manufactured products, the system structural optimization is reduced to redistribution of raw materials and the supply stream that ensure minimum deviation from the given (reference, desired) product structure under the given conditions and restrictions. The first stage consists of several levels.

The first level represents the description of the product chemical composition, and a criterion of minimum deviation P(z) from the set structure of nutritional value ingredients across the whole variety of product components is introduced for product quality assessment:

$$P(z) = \sum_{i=1}^{N} \sum_{k=1}^{\chi} \lambda_{ik} \left(z_{ik} - \sum_{j=1}^{m} b_{jk} x_{ij} \right)^2$$

with λ_{ik} — the coefficients of significance of deviations of the k^{th} index of the chemical composition in the i^{th} product determined depending on the biological value, deficiency, cost and other component characteristics.

The second level is linked with quantitative assessment of mono-structures — ingredients of the product biological value (essential amino acids, polyunsaturated fatty acids and others); that is, components of the chemical composition elements. In this case, a criterion is expressed as a sum of squared deviations of the content of mono-structure elements from their values in a certain reference balanced product (for example egg protein or breast milk):

$$P(s) = \sum_{i=1}^{N} \sum_{k=1}^{\chi} \sum_{t=1}^{T} \beta_{ikt} \left(S_{kt} - \frac{\sum_{j=1}^{m_i} a_{jkt} b_{jk} x_{ij}}{\sum_{j=1}^{m_i} b_{jk} x_{ij}} \right)^2$$

with the coefficients β_{ikt} of significance of deviation of the t^{th} ingredient of the k^{th} element of the i^{th} product.

According to the concept of the minimum degree of assimilability by the body of the elements of the product chemical composition (minimal score),

$$G_{ikt}^{\min} = \min \left\{ \frac{\sum_{j=1}^{m_i} a_{jkt} b_{jk} x_{ij}}{S_{kt} \sum_{j=1}^{m_i} b_{jk} x_{ij}} \right\}; k = \overline{1, \chi}, i = \overline{1, N}$$

which shows the minimum content relative to the reference of the t^{th} microelement of the k^{th} group in the i^{th} product.

The total losses of the biological value of product components can be used as a criterion of the system efficiency and optimization:

$$\Psi(u) = \sum_{i=1}^{N} \sum_{t=1}^{T} \left(1 - G_{ikt}^{\min}\right) \sum_{j=1}^{m_i} a_{jkt} b_{jk} x_{ij}; k = 1, \chi$$

The second stage is linked with designing structural forms of a food product.

The optimal recipe of a food product at the 1st stage does not guarantee transformation into a stable system with required structural-mechanical and functional-technological indices during technological processing.

Acquisition of certain structural forms (consistency, appearance, cohesiveness, texture and so on) by a food composition is conditioned by peculiarities of colloid-chemical processes of the «protein-protein», «protein-water», «protein-fat» and «water-protein-fat» types. It is impossible to be sure that recipe ingredients will be transformed into a stable disperse system with required properties as a result of technological processing [11].

To realize the second stage, it is necessary to have information about actual values of the functional-technological properties (FTP) of main raw materials, auxiliary ingredients, kinetics of biochemical and colloid-chemical processes (first of all, structurization) in multi-component food systems, analytical and empirical dependencies that characterize the main regularities of behavior of heterogeneous disperse systems upon variation of the physico-chemical factors.

With appearance of more and more convenient tools for processing and storage of large data, an opportunity for increasing the number of variants of using and alternatives for the development of a food product digital twin arises, which in turn, increases adequacy and validity in decision-making.

Nowadays, food product databases should contain not only information about the main indices (moisture, protein,

Table 1. The main functional-technological properties of certain types of meat raw materials [12]

Raw material type	Before thermal processing							
	Water-binding capacity to total moisture, %		Plasticity, $x10^{-1}$ m²/kg		Water absorption, % of total mass		Fat absorption, % of total mass	
	3 mm	cutter	3 mm	cutter	3 mm	cutter	3 mm	cutter
Beef, 2nd grade	78.0 ± 2.8	87.0 ± 5.0	9.74 ± 0.4	11.76 ± 0.8	56.2 ± 4.4	55.3 ± 3.8	28.4 ± 3.0	30.9 ± 1.6
Cutlet meat	85.9 ± 3.4	88.4 ± 4.6	10.6 ± 0.8	12.13 ± 1.0	52.3 ± 3.7	54.8 ± 6.2	26.3 ± 3.0	31.4 ± 1.8
Semifat pork	73.8 ± 6.0	74.6 ± 3.8	9.46 ± 0.3	11.5 ± 0.5	34.9 ± 2.3	64.2 ± 4.2	22.5 ± 1.2	28.6 ± 2.1
Fat pork	-	-	10.52 ± 0.2	12.31 ± 0.3	29.2 ± 2.4	32.2 ± 2.6	19.8 ± 2.0	23.4 ± 1.7
Mutton, single grade	70.4 ± 3.2	78.8 ± 2.6	7.8 ± 0.4	8.9 ± 0.4	40.2 ± 3.7	43.4 ± 3.4	24.9 ± 1.6	35.8 ± 1.3
Meat from beef heads	64.4 ± 1.8	68.6 ± 2.0	6.2 ± 0.2	6.6 ± 0.2	36.9 ± 1.3	37.3 ± 1.2	12.9 ± 0.9	17.5 ± 0.5
Meat from pork heads	-	-	5.8 ± 0.6	6.8 ± 0.5	26.6 ± 2.4	28.7 ± 2.1	18.8 ± 0.7	21.9 ± 1.3
Beef rumen	49.8 ± 3.7	65.4 ± 4.2	5.8 ± 0.6	7.7 ± 0.4	53.2 ± 4.4	58.3 ± 3.8	26.1 ± 2.2	37.8 ± 2.5
Beef lungs	94.3 ± 1.6	96.0 ± 1.2	11.3 ± 0.9	11.5 ± 0.8	30.6 ± 2.8	35.0 ± 4.0	25.2 ± 2.2	32.8 ± 3.1
Beef spleen	66.6 ± 3.4	64.2 ± 4.0	18.1 ± 0.4	18.8 ± 0.3	26.0 ± 2.0	29.3 ± 2.7	16.6 ± 1.1	18.2 ± 0.8
Esophagus meat	78.2 ± 3.3	80.2 ± 2.8	8.1 ± 0.6	8.7 ± 0.4	15.1 ± 1.1	16.5 ± 1.4	9.8 ± 0.9	12.2 ± 1.3
Beef lips	100 ± 0.0	100 ± 0.0	4.2 ± 0.5	4.8 ± 0.5	5.1 ± 0.6	6.1 ± 0.6	9.34 ± 0.8	9.8 ± 0.4

fat, energy value, amino acid, fatty acid, vitamin and mineral compositions) but also information about functional-technological properties of raw materials of animal and plant origin.

The data presented in Table 1 [12], which contain the main characteristics of functional-technological properties of certain types of protein-containing raw materials, can be used to determine conditions of component compatibility in a recipe, optimize a choice of an ingredient ratio with consideration for a probability of inter-regulation of properties of individual constituents and the resulting system in general.

1) a model of the water-binding capacity — $WBC = \sum_{i=1}^{N} w_i x_i$, where w_i — where is the water-binding capacity of the i^{th} recipe component;
2) a model of the fat-holding capacity — $FBC = \sum_{i=1}^{N} l_i x_i$, where l_i — is the water-binding capacity of the i^{th} recipe component;
3) a model of the water-holding capacity — $WHC = \sum_{i=1}^{N} v_i x_i$, where v_i — is the water-holding capacity of the ith recipe component;
4) a model of the ultimate shear stress — $\mathrm{USS} = \sum_{i=1}^{N} q_i x_i$, where q_i — is an index of the ultimate shear stress of the i^{th} recipe component;
5) a model of the dynamic viscosity (η) — $\eta = \sum_{i=1}^{N} \frac{V_i x_i}{\eta_i}$, where η_i — is the dynamic viscosity of the i^{th} recipe component; V_i is the volume fractions of recipe components;
6) a model of the density (ρ) — $\rho = \left(\sum_{i=1}^{N} \frac{x_i}{\rho_i} \right)^{-1}$, where ρ_i — is the density of the ith recipe component;
7) a model of the active acidity index (pH) — $pH = -\lg\left(\sum_{i=1}^{N} x_i 10^{-pH_i} \right)$, where — is the active acidity index of the i^{th} recipe component; x_i is the mass fraction of the i^{th} recipe component in the given recipes from (1) to (7).

The third stage is the determination of the organoleptic properties of a product under design by the methods of expert assessment with the control of agreement.

Therefore, analysis and control of optimality of different structural variants are carried out based on the complex simulation model of a food product, that is, on a digital twin.

Assessment of the efficiency of the developed food product is possible only upon analysis of many different indices.

It is convenient to generalize (convolve) a set of indices into the united quantitative non-dimensional index. To this end, it is necessary to introduce for each of them a non-dimensional scale, which should be of the same type for all unified indices. This approach makes them comparable.

After building a non-dimensional scale for each index, the next difficulty appears — a choice of a rule for combining initial individual indices into an overall index. There is no unified rule.

One of the most common overall indices is the Harrington generalized function. The basis for building this function is an idea of transformation of natural values of individual indices into the non-dimensional scale of desirability or preference. The desirability scale belongs to psychophysical scales.

The authors use a functional [13], an integral index in a form of an additive convolution, to assess quality and adequacy of a food product.

A functional, first of all, determines a correspondence to specified requirements by the chemical composition, functional-technological properties and organoleptic indices. A functional reflects an average weighted total deviation of actual values of condition parameters from the normative values.

With regard to weight coefficients and separation of certain groups of factors, the equation has the following form:

$$\Phi(x) = 1 - \sqrt{\frac{1}{n} \sum_{i=1}^{n} a_i \sum_{j=1}^{n_i} b_{ij} \left(\frac{x_{ij} - x_{ij}^0}{\Delta x_{ij}^k} \right)} \rightarrow max$$

where, n — is the number of the combined indices; x_{ij}, x_{ij}^0 — are the actual and desirable values; Δx_{ij}^k — is the maximum deviation from a desirable value for the k^{th} quality level; b_{ij} — is the weighting coefficient of the j^{th} parameter in the i^{th} group; a_i — is the coefficient of group significance.

A value of the quality coefficient changes from 1 upon complete agreement of the obtained values with recommended (the best quality) to 0 upon reaching the limit of the quality level (the limiting value), so that at negative values of a functional, there is no correspondence to the specified quality level.

A value of the quality coefficient changes from 1 upon complete agreement of the obtained values with recommended (the best quality) to 0 upon reaching the limit of the quality level (the limiting value), so that at negative values of a functional, there is no correspondence to the specified quality level.

To determine weighting coefficients, the method of a full factorial experiment can be used, when the following values are put into the columns of the response function y_{kr} of the r^{th} repetition of the k^{th} experiment: 1–0.7 — when a product has a very good quality level; 0.7–0.3 — good; 0.3–0 — satisfactory; 0-(–0.2) — bad; less than (–0.2) — a very bad quality level.

Conclusion

A «digital twin» of a food product is its simulation model associated with processing of a large number of information about the chemical composition, functional-technological properties and organoleptic indices. «New» simulation technologies allow engineers-technologists to use digital twins to carry out tests in the virtual world saving time, money and resources for physical scientific experiments on primary trial of recipes for new food products with complex composition and characteristics.

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Review paper

POSSIBILITIES OF ADDITIVE TECHNOLOGIES IN THE MEAT INDUSTRY. A REVIEW

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Key words: *3D food printing, meat products, food design, process parameters*

Abstract

Three-dimensional printing (3D printing) is a rapidly developing market of digital technologies with a huge potential for food production, which gives an opportunity to create new food products with the improved nutritional value and sensory profile, and adapted for a particular consumer. The review presents historical aspects of the development of the additive technologies and their classification, examines advantages and drawbacks of the 3D food printing, discusses key aspects of safety of three-dimensional food printing and probable peculiarities of their labeling, analyzes potential possibilities of using the 3DP technology for meat processing and aspects influencing the possibility of printing and following processing of 3D printed meat products.

Introduction

Additive technologies (3D printing) are one of the youngest and actively developing directions in the field of the creation of three-dimensional objects, including industrial culinary. Marketing experts believe that the prospects of this industry are extremely high. Additive printing allows combining food raw materials and three dimensional printing to produce complex shapes, texture and even tastes, which are considered either too complex for manual production or completely infeasible.

The use of 3D printing in food science includes different goals such as the novelty/enjoyment/creative activity, convenience and efficiency, health/nutrition, reduction of waste and increase in sustainability as well as reduction of hunger in the world [1].

Activation of the growth rate of additive food technologies is determined by the demand for mass adaptation for a certain consumer.

Food customization includes determination of the precise composition of particular nutrients. Consumers only have to order products that were created in strict correspondence to the requirements of their daily diet. In addition, it can allow taking into consideration specific individual requirements, for example, in case of difficulties in chewing and swallowing due to combination of different food ingredients and printing methods. Three-dimensional printing also reduces time consumption and labor costs in food manufacturing.

Additive manufacturing (AM) is the layer-by-layer building and synthesis of an object by computer 3D technologies.

Additive fabrication (AF) or technologies of the layer-by-layer synthesis is one of the most dynamically developing directions of digital production. AF (or AM) is abbreviation of a phrase accepted in the English technical lexicon, which means manufacturing products by adding material [2].

As any new technology, 3D printing has both positive and negative sides. Key problems associated with adoption of 3D food printing include definition of the term «food» by the new technology, the method of food manufacturing and limits of manipulation of edible ingredients [1,3].

The aim of the review is to show the possibilities of the 3D printing technologies with consideration for their advantages and risks for meat product development based on the assessment of the rheological and mechanical properties of raw material components and selection of technological regimes that affect possibilities of printing and the following processing of 3D printed meat products.

Main part

1. Historical aspects of the additive technology development

Two original technologies appeared in the 19th century are considered to be precursors of the modern AF-technologies [2]. In 1890, Josef E. Blanther proposed the method for making contour relief-maps — three-dimension maps of the locality surface. The essence of the method was as follows: fragments corresponding to the supposed horizontal section of an object were cut from thin wax plates along the contour lines of a topographic map; then, these plates were placed one on another in a certain order and stuck together. The «layer-by-layer synthesis» of a hill or ravine was obtained. After that, paper was placed over the obtained figures and a relief-map of an individual element of landscape was formed, which afterwards was placed in the paper form according to the initial map. This idea found practical application in the LOM-technology (Lamination Object Manufacturing) — layer-by-layer lamination or gluing of thin sheet materials with the sheet thickness of 0.051–0.25 mm.

In 1979, prof. Nakagawa from Tokyo University proposed to use this technology for quick production of molds, in particular, with complex geometry of cooling channels.

The second technology (photosculpture) was proposed by the French François Willème in 1890. Its essence was as follows: photo cameras were placed around an object or subject (Willème used 24 cameras at intervals of 15 degrees) and simultaneous photos were made with all cameras. Then

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each image was projected onto a semitransparent screen and an operator outlined the contour with a pantograph. The pantograph was connected with a cutting instrument, which removed a model material (clay) according to the profile of the current contour. In 1904, the German Carlo Baese proposed to use photo sensitive gelatin, which expanded upon treatment by water depending on the degree of illumination (exposure), in order to reduce labor intensity of this process [2].

In 1935, Isao Morioka proposed a method that combined topography and photosculpture. The method assumed the use of structured light (combination of black and white bands) to create a topographic «map» of an object — a set of contours. After that, contours were cut from the sheet material, placed in a certain order and, in such a way, a three-dimensional image of an object was generated. Also, these contours could be projected onto a screen as in the method by François Willème for the following creation of a three-dimensional image by a cutting instrument [2].

The first approximation to stereolithography in the modern sense was the idea of Otto Munz (1956), who proposed a method for selectively (layer-by-layer) exposing transparent photo emulsion. A contour (section) of an object was projected on a layer.

In 1977, Wyn Kelly Swainson proposed a method for obtaining three-dimensional objects by solidification of a photosensitive polymer at the intersection of two laser beams. Approximately at the same time, the technologies for the layer-by-layer synthesis from powder materials began to appear. In 1981, R. F. Housholder proposed a method for formation of a thin layer of a powder material by its application on a planar plate. Then, leveling was carried out up to a certain height with the following fusion of the layer. In the same year, Hideo Kodama published the results of the work with the first functional systems of photo-polymerization using ultraviolet lamp and laser. In 1982, A. J. Herbert published the work on creation of the three-dimensional models using X-Y-plotter, UV-lamp and a system of mirrors [2].

The technology of three-dimensional printing appeared at the end of the 1980s. A forefather of the industry was Charles W. Hull, a founder of the 3D Systems — a company, which became the first in the commercial activity in the field of the layer-by-layer synthesis. In 1986, Charles W. Hull proposed a method for the layer-by-layer synthesis by ultraviolet irradiation, focused on a thin layer of photopolymer resin. He also introduced into use the term stereolithography. In the same year, the engineer made the world's first stereolithographic 3D printer SLA (Stereolithography Apparatus), due to which digital technologies made a huge leap forward [2].

Approximately at the same time, Scott Crump, who later founded the company Stratasys, introduced the world's first FDM apparatus. Since then, the market of three-dimensional printing began quickly grow and was supplemented by new models of unique printing equipment. Up to the middle of the 1990s, they were used mainly in the research and development activities associated with the defense industry. The first laser machines, initially stereolithographic machines (SLA machines) and then powder machines (SLS machines), were extremely expensive and the range of the model materials was quite limited. In 1995, however, the turning point came making additive methods of production generally accessible. Jim Bredt and Tim Anderson, graduate students at the Massachusetts Institute of Technology, incorporated the technology for the layer-by-layer synthesis into an inkjet printer. That is how Z Corporation was founded. For a long time, it was considered a leader in the sphere of common printing of 3D objects. Widespread acceptance of digital technologies in the field of design (CAD), engineering (CAE) and manufacturing (CAM) stimulated the explosive character of the development of the 3D-printing technologies. At present, it is extremely difficult to indicate a field of material production, where 3D printers are not used to one degree or another [2].

2. Classification of additive technologies

In 2012, the American Society for Testing and Materials (ASTM), created standard ASTM/ F2792–12a, which gave a definition of «additive technologies». However, their rapid development required a revision of the existing standard and creation on its base of a new international standard that would allow combining world experience and creating a unified terminological and classification base. In 2015, ASTM in cooperation with the International Organization for Standardization (ISO) developed international standard ISO/ASTM 52900:2015 [4].

Standard ISO/ASTM 52900:2015 became a foundation for the first Russian standard GOST R57558–2017 «Additive manufacturing processes. General principles. Part 1. Terminology», which came into force from December 1, 2017 and contains the basic technical terms.

Technical classification is performed according to the following traits:

A. Method of article production.

For example, ASTM F2792.1549323–1 (USA) divides AT into seven subgroups:

1. Material Extrusion — material pushing
2. Material Jetting — material dispensing, jet technologies
3. Binder Jetting — binding agent deposition
4. Sheet Lamination — sheet material binding
5. Vat Photopolymerization — photopolymerization in a vat of liquid photopolymer resin
6. Powder Bed Fusion — fusion of material in a preformed layer
7. Directed energy deposition — direct energy supply immediately in the place of building.

Similar classification is given in GOST R57558–2017.

The processes of additive manufacturing are classified depending on the used material and printing type.

Liquid processes include stereolithography, fused deposition modeling and inkjet printing.

Powder materials are used in such technologies as 3D printing, selective laser sintering, direct metal laser sintering, selective laser melting, electron beam melting, direct metal deposition and laser engineered net shaping.

Taking into consideration the peculiarities of the food industry, the scientists of the K. G. Razumovsky Moscow State University of Technologies and Management believe that the most feasible in the food industry are the following technologies that have their own specific characteristics in terms of the simplicity of implementation, basic possibilities of using one or another raw material and commercial use at present and in the future [5]:

— FDM (fused deposition modeling) — modeling by the method of layer-by-layer deposition / fusing

The essence of the method is as follows: printers eject material (sauce, glaze, cheese, dough, chocolate, puree) layer by layer through a dispensing nozzle. It is possible to use several cartridges with different materials; respectively, several heads for printing will be used.

— PBP (powder binder printing) — powder-binding («drop-on-powder») printing

The essence of the method is as follows: an inkjet print head moves across a layer of powder and selectively deposit liquid binding material. Then, a thin layer of powder is evenly deposited on the treated surface and the process is repeated. With each new layer, the particles of powder adhere to each other. When the printing process is finished, unbound powder is automatically and/or manually removed and remaining powder can be reused.

In the original implementations, starch and sugar are used as a powder and water and food additives (regulators of viscosity and surface tension, dyes (for color printing)) as binding material.

— SLS (selective laser sintering)

The essence of the method is a successive sintering of powder material layers using high power lasers, which ensures partial fusion necessary for material sintering. Sintering is achieved by laying out contours incorporated in a digital model using one or several lasers. After scanning is finished, the powder bed is lowered and a new layer of material is deposited. The process is repeated until formation of a complete model. Before the beginning of printing, the consumable material can be heated to a temperature slightly below its melting point to make the process of sintering easier.

Foreign specialists also regard the above mentioned methods as the most reasonable for using in the food industry [6,7,8].

However, it is necessary to take into account that the process of three-dimensional (3D) food printing includes much more factors than the classical methods of additive manufacturing from thermoplastics considering a diversity of rheological properties of food raw materials and ingredients.

3. Advantages and problems of application of 3D food printing

Possibilities of using 3D printing in the food industry have been widely studied in the world with different goals. At present, 3D food technologies are directed at the following [1,9,10]:

— satisfaction of the human need for cognition, novelty, creativity, entertainment, enjoyment, convenience and efficiency [8,10],
— extension of sources of available food materials due to the use of non-traditional food components such as insects, high-fiber plant raw materials and by-products of plant and animal origin [8,9,11,12,13],
— development of healthy nutrition products and personalized foods with certain nutritional properties adapted to the particular human needs. Individuals with swallowing difficulties (dysphagia), which may be a result of intracerebral hemorrhage or another condition, can be classified as a targeted group. Researchers developed a method for printing different dishes (for example, cooked potato, carrot and chicken) in well-known shapes but with the texture that was specifically adapted to the needs of these patients. Printed dishes of this type can be incorporated with additional nutrients such as protein, vitamins or minerals also with consideration for patient's needs. Foreign researchers believe that his method will allow building complete individual diets that will be used, for example, by patients with special nutritional needs due to their diseases, sportsmen, the military and others [8,9,12,14];
— search for meat substitutes and methods for creating foods using alternative protein sources. Jasper L. Tran and Payne, C.L.R. [3,11] summarizing publications in the periodical press give the following citation: «To fully raise a cow for meat, you have to feed a cow 20,000 gallons of water and 10,000 pounds of grain in its lifetime. Then there's the cost of slaughtering, shipping and packaging. Our grandkids will say, that was insane. Instead, imagine the possibility of going to one's kitchen to have a 3D printer print out a customized burger.»
— use of technologies to implement the non-waste production philosophy (researchers give an example of applying additive technologies to increase food production profitability without the need to manufacture and store too many food), reduce waste, enhance environmental sustainability and prevent climate change;
— solution to the problem of food deficiency. According to Dr. Jason Clay, Senior Vice President for Market Transformation at the World Wildlife Fund «we have to produce as much food in the next 40 years as we have in the last 8,000 … By 2050 we're going to have to produce twice as much food as we do today. We need to find a way to do this more sustainably. The biggest threat to the planet is to continue producing food in a business-as-usual fashion» [3].
— reduction of transport volume in the whole world, reform of logistics facilities, logistics cooperation, reconstruction of the global supply chain [15].

Food printing dramatically changes a concept of food production and preparation as its use can change the whole process eliminating several stages from buying products to food preparation. An absence of food production and preparation means that: (1) labor costs of production are reduced, which leads to a decrease in food cost and (2) food becomes more «autonomous» as people can make any kind of food in comfortable conditions of their own kitchens being independent of food manufacturers or restaurants.

Scientists and the industry believe that is will lead to destruction of the production rules set in the epoch of the First Industrial Revolution. 3D printing and other methods of digital manufacture together will facilitate implementation of the Third Industrial Revolution. The social, economic and technical revolution of 3D printing is coming. Entrepreneurs, politicians and the society in general will face unforeseen possibilities and problems [16].

Monostori L. et al. think that when new technologies are applied, the traditional rigid, centralized and hierarchical way of production will change. They suggested that the future of the production and logistics system should be dynamic, open and reconfigurable [17].

Taking into consideration new possibilities and advantages of 3D food printing, it is necessary to note that the development of this direction also brings many new problems.

The biggest problems in 3D printing of food products are a choice of an ingredient mixture with account for their rheological properties, retention of structure precision in printing and stability of a shape of a created product, compatibility with the traditional food technology (for example, baking and drying) and printing speed. For example, traditional ingredients in cookie recipes are compatible with 3D printing, but when a recipe contains a high amount of fat, they do not retain their shape and structure after the final technological processing stage (for example, baking) [18].

Other problems with 3D printed food products are their safety and labeling [3]. The safety issues are linked with the assessment of whether 3D products can cause food poisoning of individuals or mass poisoning. Moreover, at present, there are no studies on the effect of long-term consumption of 3D printed products, which could lead to inevitable changes in the human body to adapt to a new diet of constant consumption of 3D printed food.

It is assumed that labeling of 3D-printed food will likely face problems similar to those linked with labeling of genetically modified organisms (GMO). Regardless of whether 3D-printed food is safe or not, it is not easy for consumers to identify the origin of this food. Thus, the question arises: do consumers have a right to know where their food comes from? Labeling should give an answer to the question of possible food imitation and exclude economic falsification (i. e., misleading consumers).

At the same time, it is necessary to take into account that people can be reluctant to eat 3D-printed food because they perceive it not as good as traditional food. It is quite natural that people have a cautious attitude to such sharp alterations in food production and necessary changes in their taste preferences. It is assumed that after a while the majority of people most likely will adapt themselves to new taste so as not to notice the difference. However, until the choice of access to traditional food is not completely excluded, the opposite could also be observed: people can get tired to eat only 3D printed food and return to traditional food [3].

This is a reason to raise a question: what is a probability of retention of high-quality traditional food in the future and their availability for a consumer?

Several specialists suggest that the wide use of 3D printing does not mean disappearance of the traditional technology. In the real production process, new and traditional technologies should be combined [12,15].

4. Possibilities of 3D printing in the meat industry (for meat product development)

4.1. How to create 3D-products?

In a cattle carcass, cuts that are considered suitable for production of high value steaks account only for 7.2%; other carcass parts are sold as less valuable [9]. Therefore, meat and meat product manufacturers are in constant search for new technologies aimed at improving utilization and value of meat cuts [19] to increase profitability and global competitiveness.

3D printing can present a wonderful possibility to use low value cuts and meat by-products for manufacturing personalized meat products [9].

However, to produce a 3D printed meat product with the required design, sensory profile and nutritional value, it is necessary to assess the suitability of meat paste for three-dimensional printing. The suitability of any food material for three-dimensional printing is its ability to be processed and spread by a 3D printer in a structure of a free shape after deposition, which depends on the conditions of printing and rheological properties of materials [7,9,12].

Meat and slaughter by-products are fibrous materials by their nature and are not suitable for 3D printing. They require the modification of their rheological and mechanical properties by adding flow enhancers to produce the paste-like material.

The emulsifying and gel-forming properties of food ingredients are of utmost importance for changing rheological and mechanical properties of meat paste for 3D printing. Cold-swelling hydrocolloids, such as xanthan gum, guar gum and gum tragacanth, which ensure production of heat-resistant gels, can be used to achieve modification of both rheological and mechanical properties. It is possible to use of heat-resistant binders (such as blood proteins and soy proteins), which can be added into the meat batter to improve its mechanical properties, mainly during its deposition and following processing. Their contribution to changes in the rheological characteristics of meat paste still needs to be widely studied [9].

As a fibrous material, raw meat has to be finely minced into a paste form with the controlled particle size to ensure

extrusion through the nozzle. As a rule, a particle size of paste ingredients should be significantly lower than the intended diameter of the 3D printer nozzle to prevent clogging.

It is recommended to use additives, which are necessary to easily extrude meat paste, as well as binding components to ensure adhesion of the subsequent layers after deposition. For example, gelatin added to a chicken, pork and fish slurry enhances its printability [9].

Lipton et al. (2010) assessed the suitability of turkey meat with addition of transglutaminase (TGase) as a binding material and bacon fat as a flavor enhancer for 3D printing. Transglutaminase was added to meat puree immediately before 3D printing to retain its rheological properties. Transglutaminase was investigated as a food additive that can enable creating complex geometries out of meat. Puree from turkey with transglutaminase was printed as a truncated dome and cooked using sous-vide methods. The organoleptic assessment showed that meat after cooking had proper taste and texture, but the shape was slightly distorted. In addition, the same meat paste was used to print a cube that contained a celery fluid gel [18]. Also, chicken, pork and fish in a slurry form with addition of the gelatin solution as a viscosity enhancer were 3D printed, although the ability to retain the shape after processing was not assessed [9].

Lipton et al. (2015) established that food texture can be changed either by combining materials with different textures in patterns or by changing porosity of the product printed mesostructure, while the nutritional composition is regulated by changes in its recipe [20].

For example, meat products can be printed using a multihead printer and include different ingredients placed in target locations/layers of meat paste (Figure 1), such as salt, garlic, fatty slurries and so on, which facilitate various mouthfeels and flavors.

Figure 1. Multi-material computer-aided design (CAD) model [9]

Similarly, it is possible to obtain different food designs with modified texture and the appetizing appearance that resemble the original meat product as an alternative to traditional meat products for people with chewing and swallowing difficulties.

Three hypothetical designs (Autodesk, Inc.), such as sausage, steak and beef patty, can be presented as an example (Figure 2). In such a way, recombined meat products, such as steaks, can be 3D printed as models from soft meat paste, fatty slurry and other food ingredients that ensure approximation to the taste and nutrient content of a beefsteak [9].

At present, there are many difficulties from the technical point of view, which prevent mass production of 3D printed meat products. Nowadays, the technology of meat production using a 3D printer is consisted in structuring meat products with various characteristics from basic meat blocks.

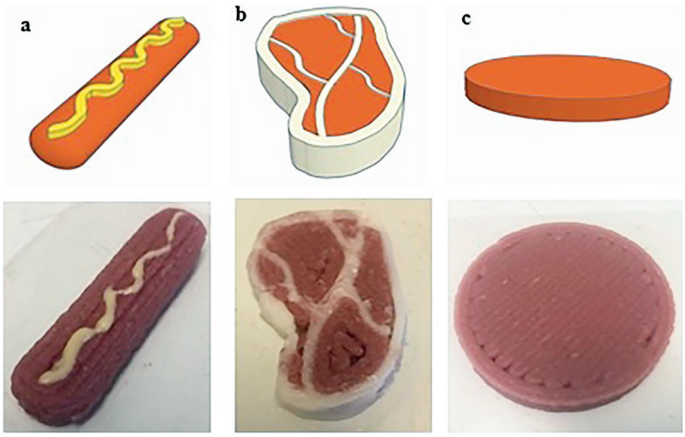

Figure 2. Hypothetical food designs for age care homes: (a) sausage, (b) steak 'recombined meat', and (c) patty [9]

Researchers from the School of Agriculture and Food Sciences, the University of Queensland (Australia) studied an effect of infill density (50%, 75%, and 100%) in the rectangular prism (40x40x10 mm) filled with a meat composition and its fat content determined by the number of layers of minced lard (0, 1, 2, and 3 layers) in the structure of the 3D meat product on the parameters of final processing of meat products cooked by the sous-vide method [21].

The meat paste base consisted of 85% minced beef and 15% water with addition of 1.5% NaCl and 0.5% guar gum used for increasing the viscosity and elasticity of a product to unsure effective 3D printing and retain the finished product structure. The printing process was performed at ambient temperature (23 ± 1 °C) using a dual nozzle model 3D printer (Shinnove, Hangzhou Shiyin Technology, China). The printing settings were determined based on preliminary experiments, as follows: 1.95 mm layer height, 1.5 mm first layer height for extruder 1 (meat paste), 1 mm layer height for extruder 2 (minced lard), 2 vertical shell perimeters, 2 solid layers on top and bottom, 20 mm/s speed, and 100% flow rate. Therefore, lard layers were printed inside a shell from meat paste to reduce fat losses during cooking.

The results of the study showed that after thermal treatment infill density had no significant effect on changes in sizes of the 3D samples of the finished meat product. The maximum values of deviations from the designed length and width were 0.6mm and 0.7 mm, respectively. The fat content did not influence the sample length and width deviation, which can be linked with the fact that the layers of minced lard were printed inside the sample perimeter minimizing the fat loss during sous-vide cooking. At the same time, significantly larger deviation for both dimensions was observed when the infill density was increased to 100%, which can be explained by a denser structure of the deposited material and consequently by an increase in the product weight. Also, an increased amount of meat paste in the product structure can facilitate deviation from the chosen configuration (shape) due to the 'extrude swell phenomenon', which may be influenced by the springiness of the material.

The infill density did not influence the deviation from the product designed height, while an inverse relationship was found when the fat content was increased. This can be explained by the lower mass of the extruded lard layer compared to the mass of meat paste, as the lard layer was deposited by the nozzle with a smaller diameter (1 mm) and a lower density of fat (0.9 g/mL (FAO/WHO Food Standards Programme, 2001)) compared to a density of the meat paste (1.106 g/mL), which was extruded using the nozzle with a diameter of 2 mm [21].

These multi-layer 3D printed samples of meat products were cooked by the sous-vide method. All samples retained their internal and external structure after heat treatment; however, partial inwards contraction was observed in the samples having two and three layers of lard and the initial fat content in a range of 8.21% to 12.65% and 14.76% to 18.97%, respectively.

In general, an increase in the fat content (or its layers) in a product led to higher cooking losses, shrinkage, increased cohesiveness, and lower indices of fat binding and moisture binding, hardness, and chewiness. In the future, the authors [21] intend to continue studying the feasibility of creating 3D printed composite multi-layer meat products with different cooking methods and conditions, analyzing microstructural changes during cooking of 3D food in order to elucidate the sensorial and textural effect on the final product.

In New York, Modern Meadows company has been working on creation of a biomaterial lineage using a 3D printer, for example, leather and, in the long-term, meat products that do not require animal slaughter [22].

Modern Meadows has proposed the new ecologically clean technology for 3D printing of meat and leather, which is much more productive and cleaner than the traditional method of animal raising.

The essence of the technology is as follows [23]. At first, living cells are taken from donor animals. The obtained material is placed into a bioreactor for multiplication. Then, the growth medium is eliminated from the «bioink» and remaining cells are put into a 3D printer to form multi-layer objects, which are again placed into a bioreactor, at this point, for maturation and generation of muscle tissue. This stage takes several weeks, after which grown meat is ready for food production.

The specialists of Modern Meadow have already achieved the first success: they printed on a 3D printer, cultivated in a bioreactor and then fried and ate a pork chop with a size of 2 × 2 cm and a height of 0.5 cm.

It should be acknowledged that printed meat products are not fully vegetarian as animal cells are used for their production. Nevertheless, bio-printing is a more humane method than animal slaughter [23].

Along with 3D -printed meat products, Modern Meadow decided to focus its efforts on the creation of artificial leather with properties of natural products, produced from animal hides. To implement its idea, the company raised $10 million for research and development.

Creation of artificial leather is quite a long process. For example, «growing» a cloth with a size of 30.5 × 30.5 cm will take about 1.5 months (Figure 3). Although, when comparing this time to 2–3 years necessary to raise an animal, this new technology appears quite attractive and promising. Moreover, as printed leather will be devoted of hair and the tough external layer, it will be completely ready for production of clothes and shoes in contrast to animal hides, which require complex multi-stage processing. The first samples of 3D printed leather were created by specialists of Modern Meadow as far back as 2012. Recently, the company has stated that it can produce leather of any kind of animals whether it is a calf, alligator or python using corresponding cells as the consumable material for a 3D printer.

Dr. Keith Belk, Professor of the Center for Meat Safety & Quality at Colorado State University, said in the interview with the portal Global Meat News that if «3D printing of meat products becomes mainstream and becomes economically and practically feasible, it can really create quite serious problems for traditional meat production» [22].

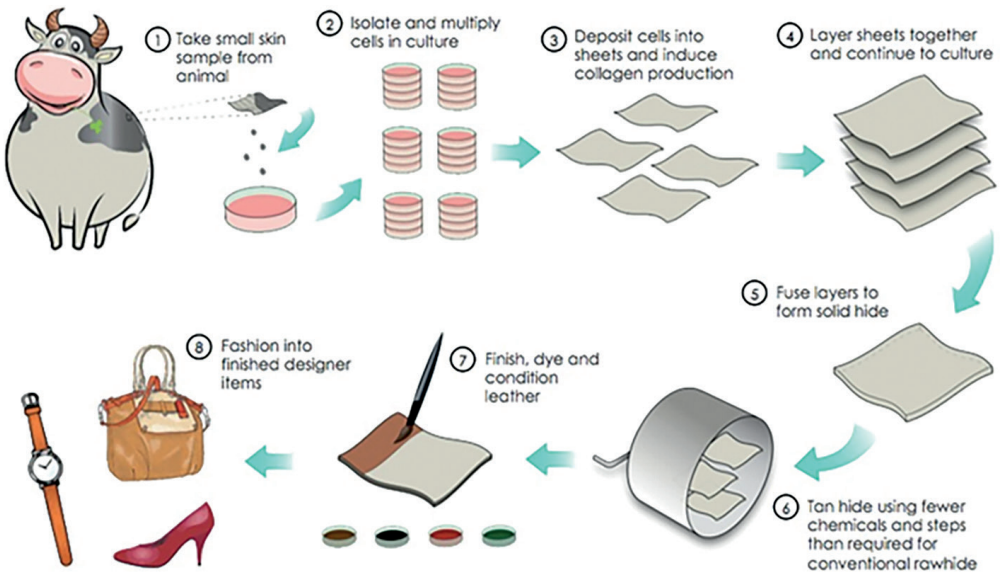

Figure 3. Figure 3. Schematic layout of 3D leather printing [23]

Dr. Joseph Sebranek, Distinguished Professor of Animal Science from Iowa State University noted that 3D printed meat products can become another category of meat products on the market along with traditional products. «While this might be an alternative,» he said, «I wouldn't expect it to replace the industry, especially with consumer interests in natural, organic products.» [22].

Prof. Keith Belk agreed that before the 3D meat printing technology can be implemented on a commercial basis, it would be necessary to solve a number of questions; although, Keith Belk noted that this technology will surely make it possible to «feed the masses,» [22].

Prof. Joseph Sebranek, however, is not so optimistic and said that one of the main problems of meat 3D printing can become «consumers' reluctance to accept 3D printed meat» rather than technical difficulties [22].

4.2. Selection of methods and conditions for quality assurance of 3D printed meat products

Several researchers determined requirements for 3D printers for meat product printing. Extruder-type 3D printers are the most acceptable for 3D printing of meat paste. It is very important to ensure the temperature control during printing, which should be less than 4 °C to prevent microbial growth. During meat printing, a temperature should be constantly controlled throughout the system — meat paste feeding, the hopper, the nozzle and the platform for meat paste deposition [9].

The critical parameters influencing the geometric accuracy of a printed construction are a nozzle speed, nozzle diameter, nozzle height (a height between the nozzle and a surface of the platform for deposition and/or a preceding food material layer), extrusion rate, and infill percentage. For example, a nozzle diameter > 2mm can facilitate extrusion of meat paste that contains bigger particle size components, such as connective tissue; however, the printing precision may be compromised due to the deposition of thicker layers. A nozzle diameter < 2mm allows production of more accurate and complex objects; however, fine emulsion-like meat pastes are necessary for extrusion through a nozzle with a lower diameter to prevent its clogging.

Likewise, an optimal nozzle height determines the accuracy and size of the printed meat product, and it is assumed that it should be equivalent to a nozzle diameter size. Due to the «extrudate swell phenomenon» [9], which is linked with meat paste springiness, a nozzle height lower than optimal can lead to scattering of the deposited flow resulting in expanded objects as compared to the desired shape. When this height is more than the optimal value it can lead to the dragging of the meat paste flow, which would not be accurately deposited on the top of the preceding layers facilitating the development of cavities inside the structure, which in turn can influence the quality of meat products after final technological processing.

If the nozzle speed and extrusion rate are not properly set, over-deposition and spreading of the meat paste flow can be observed. The nozzle speed determines the movement rate of the print head, and has to be adjusted in preliminary experiments or by calculation of the optimal nozzle speed. When a nozzle speed is optimal, the diameter of the deposited flow of meat paste is equal to the nozzle diameter. When a nozzle speed is too high, a thinner flow of meat paste is obtained and dragged, preventing the subsequent binding of layers and facilitating formation of cavities within the cross-section area of the final product. Moreover, when a nozzle speed is too low at a given extrusion rate, thicker flows are extruded and over-deposition can be observed. An extrusion rate determines the volume of the deposited material per unit time. An increase in the extrusion rate leads to production of denser products due to a higher amount of deposited meat paste [9].

Changes in the percent content of a filling material (meat paste) influence the total amount of a deposited material in the internal part of the printed product and the proportion of cavities in the final 3D printed meat product and, therefore, the conditions of the following processing. For example, the volume of cavities will determine the conditions of cooking to a certain degree of doneness as upon higher porosity in the structure, heat transfer during cooking is less intensive, which influences the moisture and fat release, and therefore, the texture of the cooked meat product [9].

By the percent content of a filling material is meant a volume (percent) of filling the chosen pattern of a three dimensional object with meat paste. For meat products, it is recommended to use 80–100%.

When choosing the above considered parameters necessary for geometric accuracy during 3D printing of meat, the economic aspect should be considered. For example, a lower printing speed and a lower nozzle diameter, as well as an increased infill percentage can lead to higher accuracy in reproduction of a product geometric shape, but longer printing time and an increase in energy consumption [9].

The other method of three-dimensional printing, which is possible to use in meat manufacture, is bio-printing. Bioprinting is a relatively novel technology based on tissue engineering and is aimed at generating raw meat tissue by printing cultured stem cells. In this method, an inkjet printer places cells into the agarose gel support structure, which is fused and forms artificial meat. After fusion, the agarose structure is removed and the tissue is subjected to low frequency stimulation in a bioreactor for maturation of meat fibers. Although, this method represents a great progress in terms of reducing slaughter of farm animals, it is still necessary to solve problems regarding its cost-efficiency, assurance of organoleptic characteristics of the final products and consumer acceptance [9].

Conclusion

3D food printing is one of the youngest technologies in the field of creating 3D objects; however, this does not prevent its development and improvement in different directions simultaneously. 3D food printing has several

significant advantages such as creation of individual food designs, personalized nutrition, simplification of the supply chain and extension of available food raw materials and ingredients. Although studies of 3D food printing have been expanding today, there are still some problems that need to be solved including an increase in print precision and accuracy by regulating a printing speed, nozzle diameter, rheological characteristics of edible «ink» for 3D food printing and other parameters, organization of production of food with certain quality and nutritional characteristics, changes in the consumer attitude to 3D foods and so on.

Studies have been carried out regarding a possibility to print meat materials such as pork and poultry meat. These studies show that addition of different food hydrocolloids into meat paste can ensure modified rheological and mechanical properties due to different binding mechanisms, increasing its suitability for printing and viability after processing. At the same time, there are no data on beef. The results of the studies on recipes to correct rheological and mechanical properties of beef paste are necessary to better understand its printability, as well as 3DP settings and conditions of following processing of printed meat products. As soon as these problems are solved, the wider use of 3D food printing is expected.

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Original scientific paper

RESEARCH OF FUNCTIONAL AND TECHNOLOGICAL PARAMETERS OF HIGH PRESSURE PROCESSED MEAT

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Key words: *meat, high hydrostatic pressure, mode, technology*

Abstract

High hydrostatic pressure (HHP) technology has been widely used in the developed countries food industry for production and preservation of raw materials and products. In our country the possibility of a new processing method is being now tested only on experimental installations. For research we selected a pressure range from 200 to 700 MPa, the exposure duration at room temperature was 20 minutes. This article presents the results of the high pressure impact on pH, water-binding capacity of broiler chickens meat, moreover comparative assessment of range of losses that occur during heat treatment and high hydrostatic pressure were analyzed. The dynamics of change of the ultimate sheer stress depending on the HHP value is shown. It is established that the new technology in the selected range does not significantly affect the pH value. However the value of water-binding capacity increases along with increasing of pressure: during processing by 200 MPa it increases by 10.5%, within the range of 200–300 MPa it increases by additional 3.0%, and within the range from 300 to 700 MPa the value increased only slightly. Significant changes were observed in the determination of losses while technological processing of meat. Thus the losses during conventional boiling of broiler chickens fillets were 28.5% higher than during high-pressure processing. It is noted that within the range of 200–700 MPa this parameter increases by only 4.8%. As the pressure increased, the texture of the meat becomes denser, as evidenced by the results of the study of the structural and mechanical properties of the raw material. Based on the results of the implemented work, it is recommended to use HHP technology within the range of 600–700 MPa, processing time of 20 min at 20 ± 1 °C for production of poultry meat products.

Introduction

The use of meat for production of various meat food products is determined by a set of functional-technological properties (FTP). They characterize the ability of the meat to retain water, fat, to form emulsions, gels, to form the structure and they determine organoleptic properties of meat products as well as the yield and losses during heat treatment.

FTP values depend primarily on meat proteins containing a large number of groups capable of interacting with water and fat molecules, as well as to interact among each other. The interaction of the protein-water system determines the following FTPs: water binding capacity, solubility, extraction and swelling.

The protein of fresh meat has maximum activity and is the most technologically advanced, forming stable systems. When exposed to high temperature, to freezing, machine processing, the stabilizing properties of the protein decrease. Therefore, the study of the functional and technological properties of meat allows managing the process into the right direction, eliminating the factor of chance [1,2,3,4,5,6,7,8].

In recent years a qualitatively new method of meat processing by high hydrostatic pressure (HHP) has emerged in the field of food production and food processing. The main objective of this technology is to obtain from protein and other substances the full-scale, high-quality products with a prolonged shelf life [9,10,11,12,13].

High pressure treatment (HP) is used in countries of Western Europe, North America and Japan, where population demands for new food products, which in the scientific literature are called new forms of food [14,15,16].

The industrial introduction of HHP technology has been rapidly developing, thus replacing a significant part of traditional food products that are produced using thermal methods [17,18]. The allowable volume of replacement is determined by the effectiveness of this processing method and the functional properties of the raw materials [19,20,21].

The quality of the finished product directly depends on the modes of technological operations. For the present day the use of HHP for the processing of food raw materials and food production is not well studies, so this research topic is relevant and actual.

The aim of the work was to study the impact of unconventional processing of HP on the functional and technological properties of poultry meat.

Materials and methods

The object of the research was broiler chicken fillet chilled down to a temperature of from — 2 °C to + 4 °C inclusive, with storage period not more than 24 hours (according to GOST 31962–2013 «Chicken meat (carcasses of chickens, chickens, broiler chickens and parts thereof)».

The experimental samples were processed with pressure at 200, 300, 400, 500, 600, and 700 MPa in five repetitions, the duration of exposure in the static mode was 20 minutes. In order to exclude the thermal effect on the product (temperature factor), the experiments were implemented at 20 ± 1 °C. To isolate the meat in the high-pressure chamber from the working fluid, samples 4 × 4 × 6 cm in size were packed under vacuum in heat-shrinkable film made of food-grade polyethylene.

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Control samples — the raw (chilled) poultry meat and boiled poultry meat cooked until culinary readiness.

The impact of HHP on poultry meat was studied on an automated high-pressure unit (AUVD), developed and manufactured at the Donetzk National University of Economics and Trade named after Mikhail Tugan-Baranovsky, which allows registering object parameters before processing; create pressure and temperature while holding the food product in a high-pressure chamber from several minutes till one day, to register volume and temperature, to reduce pressure, to study changes in objects that have been exposed to above-mentioned modes. The necessary pressure in the HP chamber is created by a hydraulic press, which transfers force to the piston of the chamber. The hydraulic unit with a pump and the press device controls the pressure in the chamber according to the commands from the personal computer located in the installation control unit.

PES-3, polyethylsiloxane liquid, which is a dielectric, does not cause corrosion of parts, pressure hysteresis, and as the working fluid reduces the likelihood of jamming. PES-3 is neutral to the researched objects, it is odorless, environmentally friendly, suitable for operation at high pressures and temperatures from — 40 °C to +100 °C, is non-combustible, has low-viscosity, has moderate compressibility due to which it accumulates relatively small elastic energy, which reduces the likelihood of serious consequences in case of the chamber destruction [22].

In this research the generally approved, accepted, standard and original research methods were used [23, 24, 25].

The pH value was determined by potentiometric method using a pH-150MI ionomer with a glass electrode with a resolution of –1.00 to +14.00 pH and an error is ± 0.05. To determine the pH an aqueous extract of muscle tissue was prepared in a ratio of 1:10 according to the method of Krylova N. M., Lyaskovsky Yu. M.

Water binding capacity was determined by pressing method according to Grau R. and Hamm R. in the modification of Volovinsky V. P. and Kelman B. Ya.

We proposed an improvement of this method: after pressing the samples, a measuring length of 1 cm was marked on the filtering paper for its further scaling. After that scanning and computer processing in the KOMPAS-3D program were performed. This program allows to determine automatically the internal and external area of the spot using scanned pattern, which improves the accuracy of measurements.

The quantitative value of the weight loss of the product (X,%) during processing was determined by the formula

$$X = \frac{(m_1 - m_2) \cdot 100}{m_1}, \% \qquad (1)$$

where m_1 — weight before technological processing, g;
m_2 — weight after technological processing, g.

The device PM-3 was used to determine the structural and mechanical parameters.

Results and discussion

The pH value is one of the main characteristics in the meat products manufacture. The pH can be used to define the quality of meat after slaughter, storage stability, and the formation of red color of meat products. Water binding capacity also depends on this parameter.

When studying the effect of hydrostatic pressure in the range from 200 to 700 MPa on hydrogen ions concentration, it was noted that HHP does not lead to significant changes in pH, which for all samples remained within the range of 5.98 ± 0.12 pH.

Water binding capacity (WBC) is one of the main FTP, which affects the yield rate of the finished products, juiciness and more, therefore we conducted researches aimed at studying the dependence of the WBC value on the processing modes of the HP.

In our research we modified the standard methodology for determination of WBC. The pressing method is based on the release of water from the experimental sample during pressing, the sorption of the released water, filtering paper and the determination of the amount of released moisture by the area of the stain that remains on the paper. Due to the fact that in practice it is difficult to determine accurately the areas of the stains from the compressed meat and adsorbed moisture, we have improved the method, which allows determining these values using computer graphics.

When determining WBC after pressure processing from 200 to 700 MPa for 20 min, significant differences of this parameter in experimental samples were revealed (Figure 1).

The WBC value for chilled meat was 62.9%. When using a pressure of 200 MPa this parameter increased by 10.5%, and when processing of meat at 300 MPa, the WBC value increases by another 3.0%. Within the pressure range from 300 to 700 MPa, the WBC value has not changed significantly.

It is possible that the increase in WBC is caused by the following changes in protein molecules: upon mechanical action of HHP on poultry muscle fibers, myofibrils are destroyed with the release of myofibrillar proteins. This is accompanied by the breaking of electrostatic bonds and the formation of ionized groups that bind water.

Based on the obtained data, it can be concluded that the emergence of additional centers accessible to water after pressure processing contributes to an increase in the WBC of poultry meat.

One of the main parameters of the feasibility of using one or another technological processing method for poultry meat processors is the determination of weight loss. By weighing the samples before and after HHP processing, it was found that the values of this parameter increased with pressure increase from 200 to 700 MPa by 4.8%, but the samples had lower values of this parameter over the whole pressure range in comparison with the boiled meat. Weight loss after processing at 700 MPa is lower by 28.5% in comparison with the thermal processing of poultry meat (Figure 2).

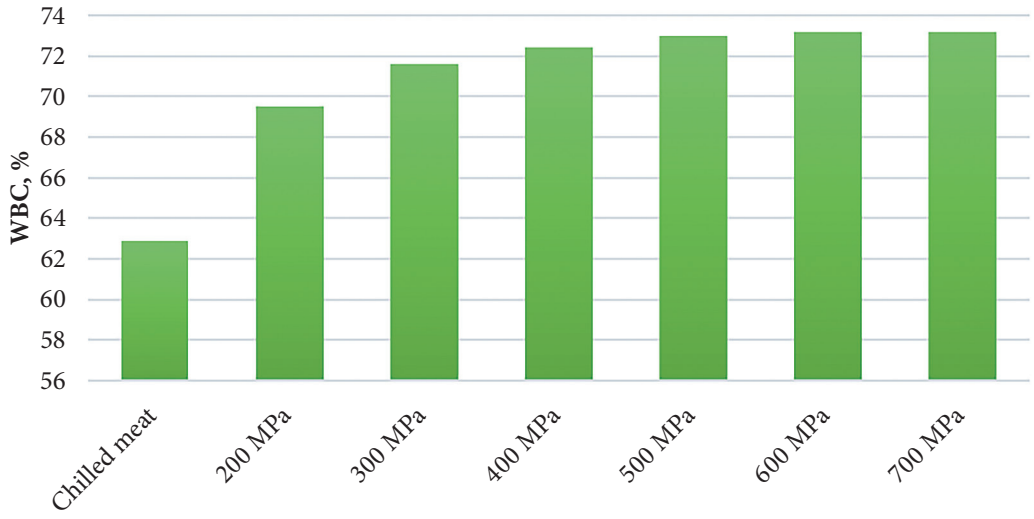

Figure 1. Changes in WBC value (%) of samples depending on pressure

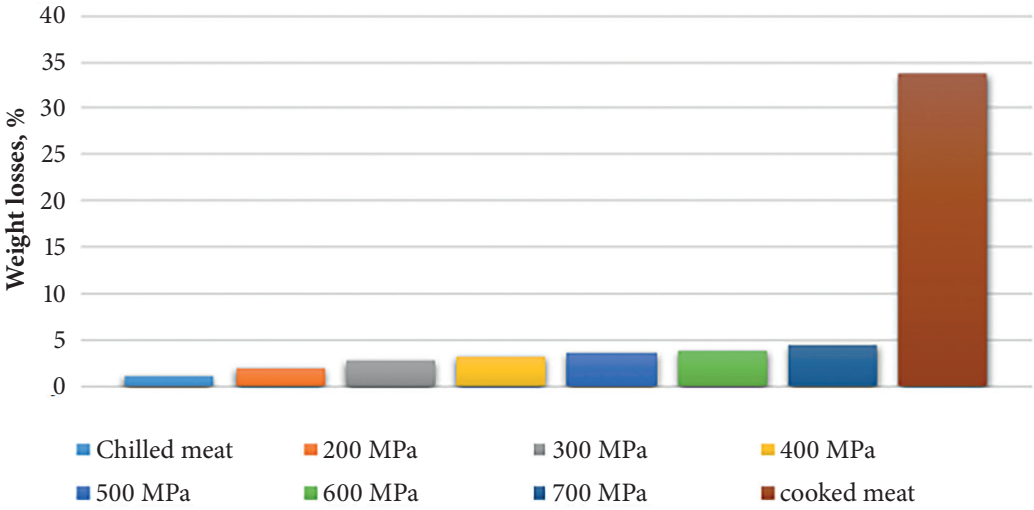

Figure 2. Change in the value of weight loss (%) of samples depending on the pressure

Structural and mechanical properties are characterized by parameters such as the texture and juiciness of the meat products. Therefore, the effect of high pressure on the ultimate shear stress was studied. The results of the study are presented in Figure 3.

Studies have shown that at a pressure of 200 MPa the ultimate shear stress is 0.41×10^{-5} Pa and gradually increases to a value of 0.54×10^{-5} Pa, which corresponds to the processing of samples at 500 MPa. Within the range from 500 to 700 MPa, a significant increase in the ultimate shear stress was observed: the value of the studied parameter increases under these pressure modes by 40.74%.

We consider that the increase of the ultimate shear stress value in the samples under study occurs due to the compaction of the meat structure under the influence of HP and the pressing out of bound moisture, depending on the

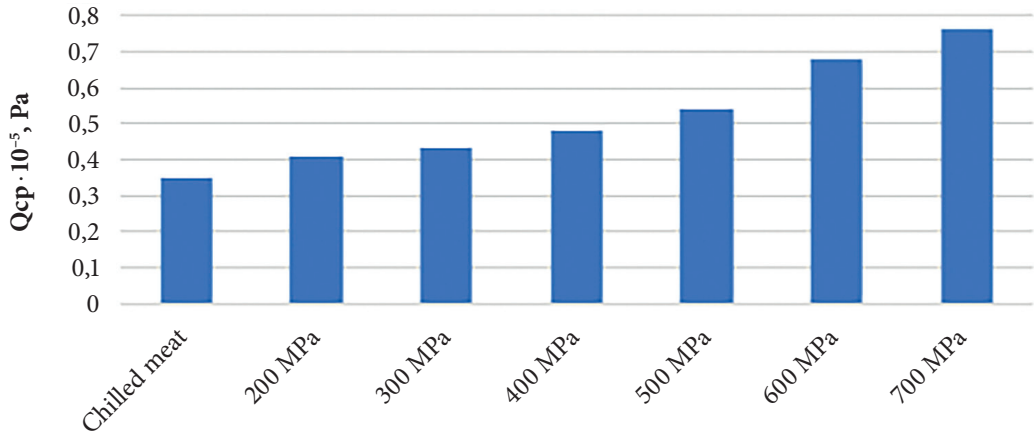

Figure 3. Changes in the value of the ultimate shear stress (Qav · 10^{-5}, Pa) of samples depending on the pressure

denaturation changes in the poultry meat proteins. Reference sources [9] indicate that the elasticity of muscle fibers increases due to the additional interaction of dipoles with water molecules, which dipoles are formed in the protein structure under the influence of HHP. Such hydration of protein molecules has an ordered structure, which density is much higher than conventional.

Considering the results obtained and previous [11] it is possible to recommend for the production of finished products from poultry meat the HHP range from 600 to 700 MPa, processing time of 20 minutes.

Conclusion

As a result of studies the significant differences in the water binding capacity value were revealed: when using a pressure of 200 MPa this parameter increased by 10.0%, while processing at 300 MPa WBC increased additionally by 3.0%. In the pressure range from 300 to 700 MPa, the value of the water binding capacity has not changed significantly.

It was proved that the weight loss increases with pressure increase from 200 to 700 MPa by 4.8%, and after processing with 700 MPa this weight loss parameter is lower by 28.5% in comparison with weight loss after heat treatment of poultry meat.

The ultimate shear stress gradually increased within the range from 200 to 500 MPa by 24%. In the range from 500 to 700 MPa, a significant increase of 40.74% was observed, which may indicate tissue compaction caused by HHP processing.

Thus the processing of broiler chicken fillets with high pressure within the range from 200 to 700 MPa for 20 minutes at +20 °C improves the structural-mechanical and functional-technological properties. This technology reduces the amount of loss, compared with heat treatment (boiling), which is important for determining the yield rate of finished products in the processing of raw material of this type.

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Original scientific paper

CALCULATION OF HEAT CAPACITY IN MEAT DURING ITS FREEZING CONSIDERING PHASE CHANGE

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Key words: *crystallization, meat freezing, crystallization model, freezing point coordinates*

Abstract

As a consequence of insufficient study of water phase change in meat accompanied by water crystallization, its modeling is currently based on the empirical dependence of the frozen water portion on temperature. Such model does not allow answering a number of questions such as of metrological order, and also of physicochemical interpretation of processes occurring in meat during water crystallization. In this paper, we propose an approach to modeling the phase change process of meat during its freezing on the basis of the phonon theory of Debye crystallization, which allows to obtain physically justified dependences of heat capacity on temperature in the phase change region. The obtained dependences may serve as a simple method for calculating the heat capacity of meat in the temperature range of 113 K to the cryoscopic temperature of the given meat type, or as a basis for the analysis and correction of factors affecting the meat freezing in the temperature range of the phase change.

Introduction

Most scientists in the field of food refrigeration [1,2,3,4,5,6] believe that the calculated dependence of the specific isobaric heat capacity of food products is subject to the additivity law and may be expressed as follows:

$$c = g_1 \cdot c_1 + g_1 \cdot c_1 + ... + g_n \cdot c_n \quad (1)$$

where

g_1; g_2 … g_n are mass fractions of the mixture ingredients;
c_1; c_2 … c_n are specific heat capacity factors of the ingredients.

For meat and dairy products, to calculate the specific heat capacity, Latyshev V. P. et al. [5, 6] proposed a temperature dependence of the additive type, where the product is considered as a three-ingredient mixture, i. e. solids, water (ice) and fat:

$$c_p = c_{sol} \cdot \xi_{sol} + c_{fat} \cdot \xi_{fat} + \xi_{wat}\left(c_{ice} - L\frac{d}{dt}(\omega)\right) \quad (2)$$

where

c_p; c_{sol}; c_{fat}; c_{ice} are specific isobaric heat capacities;
ξ_{sol}; ξ_{fat}; ξ_{wat} are mass fractions of solids, fat and water, respectively;
L is specific heat of crystallization, J/kg;
ω is portion of frozen-out water, T is temperature, K.

All members of the dependencies are empirical, which suggests the need to measure heat capacities of many ingredients, including portions of frozen-out water.

The value of heat capacity in the phase change region is not included in equation (1) due to its general nature. In equation (2), this drawback is eliminated, but the member considering heat capacity of phase change is based on the derivative of the frozen-out water portions, which is determined by empirical methods that do not have a satisfactory physicochemical basis [3,4,5,11]. In this regard, difficulties arise in determining the extreme values of heat capacity, as well as in determining the start of melting or the end of freezing.

Recently, several studies were conducted on processes of freezing and thawing, considering their effect on product quality [11,12,13,14,15,16,17,18,19,20].

The method for modeling and analysis of phase change in meat during its freezing proposed in this paper is based on other methods not previously used. Dependence determining for the specific heat capacity proposed by Debye was carried out using the Einstein-Planck dependence obtained for gases. But as shown by Debye with some assumptions, this dependence may also be applied to crystalline bodies. This approach makes it possible to clarify the temperatures of the beginning and ending of the phase change process, as well as to identify energy factors affecting the process.

Materials and methods

In this work, the experimental basis for modeling the meat freezing process is the results of meat thermophysical characteristics study obtained on NETSCH 204 F1 differential scanning calorimeter (DSC). The ability to increase the reliability of measurements of meat specific heat capacity by differential scanning calorimetry methods is realized by τ–R correction [9]. A comparison of the results of such measurements with similar measurements using an adiabatic instrument [5,7] indicates almost complete agreement.

Determination of the meat cryoscopic temperature is carried out by OSKR-1 osmometer cryoscope, which is included in the State Register of Measuring Instruments of the Russian Federation with No. 42519–09. Specification of OSKR-1 are shown in Table 1.

Table 1. Main specifications of OSKR-1

Parameter	Tolerance
Range of freezing temperature measurement:	0 to –3.720 °C
General absolute tolerance in temperature measurement	
— in the range of 0 to –0.930 °C:	±0.002 °C
— in the range of –0.930 to –3.720 °C:	±0.010 °C
Sample volume, not less than:	0.3 ml

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The research objects were:

1) NOR grade beef. Beef samples were obtained at meat processing plants in the Moscow region immediately after slaughter and production. Samples were taken from *M. longissimus dorsi*;
2) Pork samples were obtained at meat processing plants in the Moscow region immediately after slaughter and production. Samples were taken from pork *M. longissimus dorsi*. All samples were of NOR grade.

The study of the phase change in meat near and at the cryoscopic point in theoretical terms is associated with the singularity of modeling functions. Whereas in meat, this temperature range is the least studied regarding the physicochemical parameters of freezing process [10]. The proposed model of the meat freezing process based on the Debye quantum-mechanical approach (phonon theory of thermal radiation [12, 13]) allows the analysis to be carried out step-by-step over small temperature ranges near and at the cryoscopic temperature point.

Results and discussion

Equation of the crystal internal energy according to the Debye hypothesis is as follows:

$$U = \frac{3Nh\nu}{2} + 3Nh\nu\frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}, \quad (3)$$

where

U is internal energy of a crystal atom, J;
N is the number of atoms in the ice crystal ($N \sim 10^{25}$ kg^{-1}) in the Einstein-Planck equation, which was converted by Debye to apply the description of the crystalline body energy;
h is the Planck constant, h = 6.626·10^{-34} J·s;
ν is the frequency of atom vibrations in the crystal, s^{-1};
k is the Boltzmann constant, J/K;
T is the temperature by the Kelvin scale.

It is advisable to consider the energy of the crystallization process in the accepted interpretation as a function, the argument of which is the temperature deviation from the cryoscopic point, i. e. (T_{kr} — T). Then the equation (1) is as follows:

$$U = \frac{3Nh\nu}{2} + 3Nh\nu\frac{e^{-h\nu/k(T_{kr}-T)}}{1 - e^{-h\nu/k(T_{kr}-T)}} = \frac{3Nh\nu}{2} + 3Nh\nu\cdot\frac{e^{-\theta/\psi}}{1 - e^{-\theta/\psi}}, \quad (4)$$

where:

$\theta = h\nu/k$; and $(T_{kr} - T) = \psi$.
θ is a coefficient in degrees; in Debye's work it is called the characteristic temperature [12].

The heat capacity of the test sample is the derivative of (4) with respect to ψ. Considering that, for small values of ψ near the cryoscopic point, $e^{-(\theta/\psi)} << 1$, we will have

$$c = 3Nk\cdot\left(\frac{\theta}{\psi}\right)^2\cdot e^{-\frac{\theta}{\psi}}, \quad (5)$$

where

N is the number of ice crystallization centers per mass unit of the product, N = 10^{25}, it is measured in kg^{-1};
μ is the coefficient of the order of unity correcting the N for a certain type of meat (beef, pork, etc.);
T is the temperature by the Kelvin scale, K.

As will be shown below, equation (5) is valid in the following interval:

$242 < T < T_{kr}$ by the Kelvin scale and $t_{kr} << t << 0$ °C;

$0 < \psi < 273$ K.

In the research laboratory of food products thermophysical properties, the All-Russian Scientific Research Institute of Refrigeration Industry, the analysis was carried out of the phase change process when freezing beef and pork using transformed dependence (5). In the expanded semi-empirical version, the equation is as follows (6):

$$c = \mu\cdot N\cdot k\cdot\left(\frac{\theta}{T_{kr} - T + \delta}\right)^2 e^{-\left(\frac{\theta}{T_{kr}-T+\delta}\right)} + B\cdot 10^{-3}\cdot T, \quad (6)$$

where

δ is the coefficient for deviation of the temperature of the water crystallization onset (during the process of transformation into ice) from the temperature of the heat capacity peak in the process of phase change, K;
B is an empirical coefficient in J/kg·K^2 characterizing the contribution of heat capacity of anhydrous ingredients.

Dependence (6) allows to determine the heat capacity of meat in the phase change region with an error of ± 3.5% in the temperature range of $242 \le T \le T_k$. The peaks of the calculated curves correspond to the maximum experimental values of meat heat capacities: 300 kJ/kg·K and 240 kJ/kg·K for beef and pork, respectively. The deviation of the temperature of the maximum calculated heat capacity from the corresponding maximum of the experimental heat capacity is 0.1 K both for beef and pork. Meat moisture is significant for determining heat capacity and must be kept within the limits specified for given meat grade.

The values of μ, θ, δ coefficients and cryoscopic temperature T_k for beef and pork of NOR grade are shown in Table 2.

c_{max} is the maximum value of heat capacity at the peak of phase change, kJ/kg·K.

Table 2. The values of the coefficients for equation (6)

Meat type	θ	T_{kr}	μ	δ	B	c_{max},
Beef	0.55	272.19	1.335	0.35	$7.5\cdot10^{-3}$	300
Pork	0.71	272.0	1.06	0.5	$6.7\cdot10^{-3}$	240

In the rest of the temperature range of 110 K to 242 K, the deviations of the calculated values of heat capacity do not exceed 3%. The tabular values of δ parameter slightly exceed the experimentally obtained data corresponding to the curve segment for the crystallization onset, i. e. the experimental value is δ = 0,01 K. In our opinion, such deviation from the theoretical curve may be due the methods and accuracy of temperature measurement in a frozen product during crystallization.

The proposed interpretation of the model for water crystallization in meat allows to identify the relationship

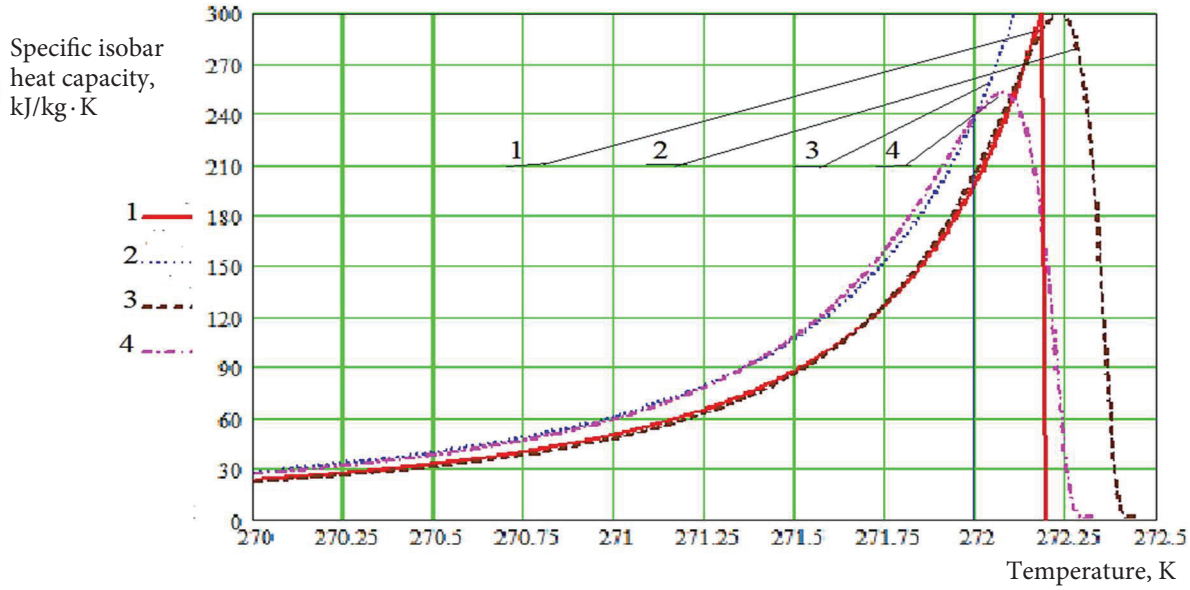

Figure 1. Shows the diagrams for obtained by differential scanning calorimetry (DSC) using DSC204 F1 device (curves 1 and 3) and diagrams obtained by calculation according to equation (6) (curve 2 — beef, curve 4 — pork).

between the heat capacity of meat and the characteristic Debye temperature (θ), i. e. the frequency of phonon waves. In addition, it seems to be possible to assess the degree of water crystallinity in meat characterized by the N·μ parameter.

For determination of heat capacity of NOR grade beef and pork in the temperature range of phase change, equations (7) and (8) are proposed, respectively:

$$C_{beef} = \frac{185,47}{(T_{kr} - T + 0,777)} + 7,4 \cdot 10^{-3} \cdot T; \quad (7)$$

$$C_{pork} = \frac{227,7}{(T_{kr} - T + 0,777)} + 6,66 \cdot 10^{-3} \cdot T \quad (8)$$

To apply these equations, it is sufficient to determine only the cryoscopic temperature of the meat. In the indicated temperature range, the deviation of the heat capacity calculated values does not exceed ± 3.5%.

In [14], the results of comparing the experimental and calculated determinations of the cryoscopic temperature depending on beef moisture content are presented (9). In the range of moisture content of 0.6 ≤ w ≤ 0.8 with an error of ± 0.2 K

$$T_{kr} = 256,64 + 35,0 \cdot w - 19,3 \cdot w^2 \quad (9)$$

Equation (9) allows to conclude that the heat capacity of the studied beef, in fact, depends only on moisture content and temperature.

Such a fairly accurate determination of the heat capacity values when compared with the curves obtained experimentally by the DSC method using the τ-R correction allows to identify the points of the phase change termination and continued cooling of meat with water contained in it that is not subject to freezing.

The experimental DSC curves of beef and pork heat capacity shown in Figures 2 and 3 have a noticeable break point, i. e. sharp change in curvature. At these points, the interpolation curves describing the experimental ones with high accuracy disagree with the latter. In the temperature range of 110 K to 242 K, experimental DSC curves are described by polynomials (9) and (10) with the high accuracy of ± 3%.

The coordinates of the intersection points (see Figures 2 and 3):

— for beef 243 K;
— for pork 242 K.

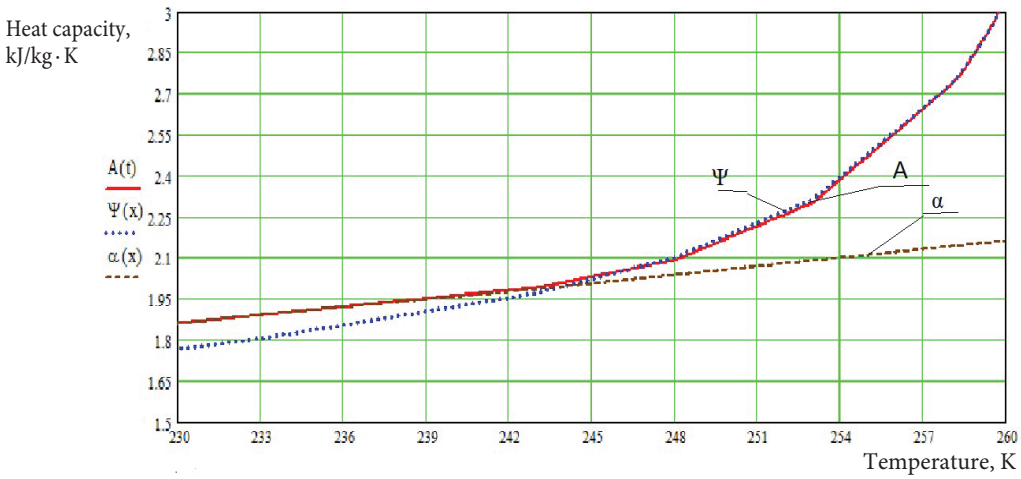

Figure 2. Beef heat capacity in the temperature region of the transition from crystallization ending to cooling of the frozen product: A is the DSC curve; α is the calculated heat capacity curve below the phase change region; ψ is the calculated curve of the phase change region

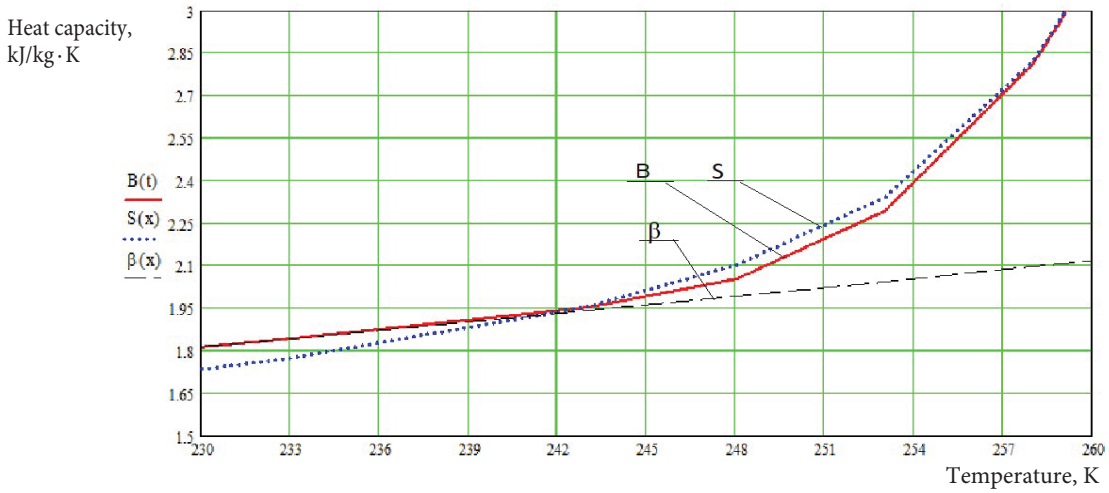

Figure 3. Pork heat capacity in the temperature region of the transition from crystallization ending to cooling of the frozen product: B is the DSC curve; S is the calculated heat capacity curve of the phase change region; β is the calculated curve below the phase change region

Dependences for heat capacities:

beef

$$C_{beef} = 0{,}548 + 1{,}85 \cdot 10^{-3} \cdot T + 1{,}68 \cdot 10^{-5} \cdot T^2 \qquad (9)$$

pork

$$C_{pork} = 0{,}7 + 0{,}15 \cdot 10^{-3} \cdot T + 1{,}9 \cdot 10^{-5} \cdot T^2 + \\ + 0{,}55 \cdot 10^{-8} \cdot T^3 + 0{,}1 \cdot 10^{-11} \cdot T^4 \qquad (10)$$

In Figures 2 and 3, these dependences are represented by α and β curves:

It must be considered that the use of the indicated equations is possible only within the temperature range of $113\ K \le T \le T_{Ophase}$, K; T_{Ophase} is the temperature of the phase change ending.

Conclusion

Semi-empirical transformation of the Debye theoretical provisions on the process of solids crystallization allowing to determine the dependence of their heat capacity on temperature made it possible to obtain the calculated dependences of beef and pork heat capacity in the temperature range of phase change during meat freezing.

It is shown that the transition from phase change during meat freezing to stationary meat cooling has clear boundaries with stationary coordinates. These coordinates are determined for beef and pork of NOR grades.

It is shown that beef and pork heat capacity may be calculated based on only two thermophysical characteristics of meat, i. e. moisture content and cryoscopic temperature.

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Original scientific paper

DEVELOPMENT OF LITHIUM–CONTAINING FEED ADDITIVE AND ITS USE FOR FORTIFICATION OF CHICKEN BROILERS MEAT AND BY-PRODUCTS

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Key words: *feed additive, lithium, broiler chickens, meat, minced meat, fortified food products*

Abstract

The article presents the researches on the development of a feed additive for broiler chickens, including succinic (amber) acid, zinc sulfate, manganese sulfate, copper sulfate, lithium carbonate, L-carnitine, betaine. It was found that the introduction of the developed feed additive to mice food in a dose exceeding 5000 mg / kg per body weight did not affect the general condition of the animals. The experimental results did not allow determining the LD50 of the researched feed additive. The lithium-containing feed additive does not have chronic toxicity, does not cause pathological processes in the internal organs of mice and it belongs to hazard class IV (low-hazard substances). It was found that the introduction of a feed additive in amount of 2,350 g per 1 ton of mixed forage for broiler chickens (the concentration of ionized lithium is 66 mg per 1 kg of feed) allows increasing the content of lithium in cooked meat, minced meat and by-products in comparison with samples of products taken from the experimental group. The lithium content in boiled white meat is 0.418 mg / 100 g, which is 211% higher than in the control sample; 0.452 mg / 100 g in boiled red meat which is 426.4% higher than in the control sample. Eating of 300 g of boiled chicken meat fortified with lithium obtained in the process of broiler chickens cramming, this meat provides the recommended daily dose of the specified trace element. The obtained data allow using the raw meat and by-product for the production of lithium fortified food products.

Introduction

Food fortification with essential elements is a reliable way to prevent nutritional-related diseases. Particular attention is paid to the development of the mass-market food fortified with irreplaceable micronutrients in a biologically accessible form, which is refereed to meat products also.

One of the directions of scientific activity in fortified food technology is the introduction of a biologically active component at the stage of production of food raw materials — i. e. biological fortification when growing crops or cramming/fattening farm animals (in vivo formation of the raw materials composition). The use of mineral zinc-containing fertilizers when growing plants allows increasing the content of this microelement in plants and increases its bioavailability [1,2].

Gyro T. M. and Gorlov I. F. (2018) developed a method for fortifying of mutton by incorporating organic forms of iodine and selenium into the animals forage in the form of feed additives [3].

One of the important trace elements in human nutrition is lithium.

Lithium belongs to the range of essential elements, it prevents stress development, reduces the risks of oncology, prevents the formation of atherosclerotic lesions in blood vessels and is characterized by other pharmacological features. The therapeutic doses of lithium are 70–280 mg per day. The recommended prophylactic dose is up to 5.6 mg of elemental lithium per day or 600 mg of lithium carbonate 3–4 times / day [4]. The maximum daily intake dose for adults is 2.4 g. Lithium is a part of dietary supplements: KAL, Lithium Orotate 5 mg, 60 VegCaps, Solaray, Lithium Aspartate 5 mg, 100 Capsules [5].

In 1985 the Environmental Protection Agency (EPA) of the United States of America proved that the daily intake of Li by the adults weighing 70 kg should be 650–3100 mcg. While monitoring the diets of adult people it was found that in East Germany the average lithium intake is 0.85 mg / day, in the USA — 2.0 mg / day. But in certain regions of the planet the intake of lithium at a dose of 10 mg per day does not cause any negative consequences. It is currently accepted that a vital dose of lithium for an adult weighing 70 kg is 1 mg / day. This dose provides important neurogenesis processes, and also protects neurons from toxic substances and influences the activity of stem cells at the level of nerve tissue and bone marrow [6].

In psychiatry lithium salts are used in high doses — from 600 to 2100 mg per day. In equivalent of ionized lithium this dose ranges between 110 and 400 mg. High doses lithium therapy of pregnant women does not affect the intrauterine development of the fetus; there is also no reason to stop taking lithium-containing pharmacological agents during breastfeeding [7].

The aim of the research is to develop and evaluate the toxicity of the lithium-containing feed additive «Peak

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Antistress» and its use for broiler chickens meat and by-products fortifying.

Materials and methods

The pilot batches of the «Peak Antistress» feed additives were produced in the laboratory of the innovative research center of the South Ural Agricultural University by mixing the components, their grinding and evaluating the stability of the mixture. Before application each experimental batch underwent the solubility test and toxicity assessment in white mice and rats.

The toxicological properties of the «Peak Antistress» feed additive were studied by determining the parameters of its acute and chronic toxicity. Acute toxicity experiments were done on white nonlinear mice weighing 19–22 g in July-August 2018 at a temperature of 14 to 28 °C. Mice were kept indoors in standard cages. Light mode: 14 hours of light, 10 hours of dark. The animals were fed in accordance with generally accepted diets and feeding standards. The selection of the method of introduction of the additive into the body was determined by the physicochemical properties of the biologically active feed additive «Peak Antistress», as well as the methods of introduction of feed additives into the body of animals. The insolubility of the components of the feed additive does not allow using the parenteral routes of the feed additive administration. The dose of the feed additive for the initial administration was selected in the basis of body weight, and in all experiments it was more than 5000 mg per 1 kg of live weight.

The toxicity was studied according to the «Methodological guidelines for determining the toxic properties of drugs used in veterinary medicine and animal husbandry». In this case the most acceptable way to introduce a feed additive into the body of mice is via pills.

Mice were divided into two groups of 10 animals in each. The first group is experimental one, the second is control one. The experimental group was given pills weighing 0.5 g, 1 pill to each mouse. Each pill contained 0.115 g of «Peak Antistress» supplement, and wheat flour was used as filler. The pills were dried by natural ventilation and temperature. The control group of mice used a placebo consisting of wheat flour only. Before the pills administration the mice were not fed for one day.

The chronic toxicity of «Peak Antistress» feed supplement was studied in 30 male mice. The mice were divided into 3 groups of 10 animals each. The first group is control one, the mice of the second group were given «Peak Antistress» at 5 therapeutic doses, which are 5% of the feed weight or equal to 6 grams of «Peak antistress» per whole group, which it its turn is 0.6 grams per head. The third group was given the feed additive in a dose 10 times exceeding the therapeutic dose, or 10% of the feed weight or 12 grams per whole group, which is 1.2 grams per head. The feed additive was given in the form of pills, divided by a multiple of 10 for more uniform eating by mice. The control group received a placebo consisting of pills without the studied feed supplement. The drug was given for 30 days.

Before the experiment and on the 30th day of the experiment the mice were weighed. On the 30th day of the experiment, blood samples were taken and autopsies were made on experimental and control groups mice, their internal organs were weighed.

6 mice from each group were sacrificed by incomplete decapitation.

The mass of the liver, heart, kidneys and spleen was determined using torsion weights. After the autopsy the organs were isolated by removal the associated tissues. Large vessels were cut off from the heart, coagulated blood was removed from the cavities, the liver was weighed without a gall bladder, and the kidneys were weighed without a capsule. To remove blood organs were washed in physiological saline of sodium chloride, and then dried up with filter paper. Having obtained absolute indicators of organ weight we determined the relative mass (weight coefficients), which are expressed as ratio of the organ weight in grams to the body weight of the animal, expressed in kilograms.

Lithium concentration in meat, minced meat and by-products was determined by atomic absorption spectroscopy (AAS). Sample were prepared for AAS determination of metals content by dry mineralization according to the guidelines for atomic absorption methods for the determination of toxic elements content in food products and food raw materials (refer to the standard method of the State Committee of Sanitary and Epidemiological Surveillance of the Russian Federation (GKSEN RF) No. 01–19 / 47–11–92 dated from 25 December 1992). Meat, minced meat, by-products samples were ground, mixed and dried in an oven at a temperature of 100 °C. Meat samples were obtained by grinding the carcass and obtaining minced meat including muscles, skin and bones to obtain data on the average lithium content in the poultry carcass. A 100 g sample of mincemeat was burned in a muffle furnace with step-by-step heating (50 °C every 0.5 hours) up to 500 °C. The ash was moistened with a HNO3 solution in a 1:1 dilution ratio and dried up. The dry residue was diluted with 1N solution of HCl, filtered through a «blue ribbon» filter and the volume of the acid extract was adjusted to 25 ml. The metal content was determined on a flame-absorption spectrophotometer «AAS-1» («Karl Zeiss Jena», Germany). The state standard reference sample of lithium ion was used as calibration solutions. LT-6M lamp from LLC «Technoquant», KORTEK with a wavelength of 670.8 nm was used for determination of lithium content.

Results and discussion

The developed feed additive includes succinic (amber) acid, zinc sulfate, manganese sulfate, copper sulfate, lithium carbonate, L-carnitine, betaine in the following proportions: succinic (amber) acid 37.0–38.0; L-carnitine 5.0–6.0; copper sulfate 2.6–2.8; zinc sulfate 11.5–11.7; manganese sulfate 11.5–11.7; lithium carbonate 16.5–16.7; betaine 14.0–15.0.

It is advisable to consider the effect of biologically active substances that are part of the developed feed additive «Peak Antistress» on the body of poultry.

Succinic acid is a universal intermediate metabolite formed during the interconversion of carbohydrates, proteins and fats, and an antioxidant. It helps to strengthen the central link of intracellular energy — it increases the oxidation of succinic acid and the activity of succinate dehydrogenase of mitochondria respiratory chain; provides significant acceleration of ATP formation and its reducing equivalents, as well as stabilization of the membrane potential of both mitochondrial and cell membranes. Succinic acid compounds are the adaptogenes for hypoxia and intoxication. In poultry farming the succinic acid is recommended to mitigate the effects of various kinds of poultry stresses, it is used as growth and productivity stimulator, as well as an immunity protector [8,9].

The anti-stress activity of certain trace elements and their salts is proven. In particular the efficiency of lithium as anti-stress drug in industrial poultry farming is known [10,11,12,13].

Zinc is part of more than 200 metal enzymes, it influences on cell growth and division, skin and feather condition, osteogenesis, wound healing, reproductive function, immune system, cellular respiration, brain development, behavior, etc. Zinc deficiency causes growth stasis, testis atrophy, decreased egg production, infringement egg shell formation [14].

Manganese in birds activates numerous enzyme processes, influences blood formation, acts as antioxidant, takes part in fat utilization, counteracts liver degeneration, improves the quality of egg shells, improves the condition of embryos, affects the action of vitamins B, E, C and minerals — iron, calcium, phosphorus, improves the functioning of the endocrine glands, helps to maintain reproductive function. It was found that in case of manganese content decrease in a body, the process of ossification increases. Lack of manganese leads to a decrease in insulin synthesis, decrease or loss of reproductive ability, anemia, infringement of bone formation processes, i. e. promotes the development perosis disease. In an adult poultry herd the egg production and hatchability are reduced. Being an integral part of metalloproteins, copper regulates the oxidation-reduction processes in the body. As part of the hormones, copper affects the metabolism, growth and development, the content of vitamin B_{12} and C in the liver, enhances the action of insulin and pituitary hormones. As part of the enzymatic link of the antioxidant system, copper exerts a pronounced effect on processes of lipid peroxidation and the undesirable formation of proteins oxidative modifications [15].

L–Carnitine is a natural compound that takes a key place in animal energy metabolism. Lack of this substance leads mainly to a weakening of the conversion of energy and membrane functions. The main role of L-carnitine in energy production is the delivery of fatty acids from the cell cytoplasm to the inner space of mitochondria, moreover it participates in ketones metabolism of a body, in the regulation of glycogen synthesis and ATP formation, it stimulates the oxidation of acetoacetate, and is involved in ketogenesis and thermoregulation in fatty tissues. The use of carnitine in laying hens feed makes it possible to obtain and increases hens preservation in the productive period by 2.8%, increases egg production rate by 2.5% [16].

Betaine helps maintaining the osmotic balance in the intestines and cells exposed stress, prevents disturbances caused by osmotic shock at high temperatures, and reduces the negative effects of feed stressors and mycotoxins [13].

The components, that make up the feed supplement, complement and synergistically enhance each other's action — the pronounced anti-stress effect of trace elements is observed: lithium, copper, manganese and zinc is enhanced by osmoprotecting betaine and antioxidant activity of succinic acid; succinic acid, L-carnitine, lithium carbonate, zinc sulfate, manganese sulfate and copper sulfate have pronounced effect on metabolism, have adaptogenic properties and allow mitigating the body's costs, which increase significantly along with the development of stress.

The feed additive «Peak Antistress» looks as a white powder with inclusions of tiny grains of different colors– blue, pink. The additive is poorly soluble in water.

The experiment showed that the introduction of the «Peak Antistress» feed additive to mice in a dose exceeding 5000 mg / kg body weight did not affect the general condition of the animals. The experimental results did not allow determining the LD_{50} of the researched feed additive.

Measurements of the live weight of mice before and after the experiment (refer to Table 1) in the experimental group correspond to the indices of the control group and prove the absence of a pronounced toxic effect.

Table 1. Change in live weight of mice before and after the experiment

Group	Experimental group	Control group
Before the experiment, g	21.00 ± 0.22	21.28 ± 0.24
After the experiment, g	21.66 ± 0.25	21.91 ± 0.21
Difference, g	0.66 ± 0.34	0.63 ± 0.32
Difference,%	3.05	2.88
Before the experiment, g	0.10	0.10

While determining the chronic toxicity no animals died. Appearance and behavior were consistent with the norm and did not differ in the mice of the experimental and control groups. Data on changes in live weight of white mice before and after the experiment are shown below in Table 2.

Table 2. Change in live weight of mice before and after the experiment

Group	1 Control group	2 Experimental group	3 Experimental group
Before the experiment, g	21.3 ± 0.59	21.5 ± 0.90	22.0 ± 0.86
After the experiment, g	23.7 ± 1.21	25.1 ± 1.34	24.6 ± 1.23
Difference,%	10.1	16.7	10.6

Intergroup differences before and after the experiment are not pronounced. Comparing after the experiment the parameters of the control group and the first experimental group, it is necessary to note that the difference is statistically significant and is P = 0.029872. When comparing the control group and the third group, the difference is not statistically significant and is P = 0.109371. This indicates a stimulation of live weight gain in mice that received the «Peak Antistress» dietary additive at a dose of 5% of the feed weight, in the group where the «Peak Antistress» was given at a dose of 10% of the feed weight no similar effect was found. Estimating overall body weight indices, it is necessary to note that «Peak Antistress», when administered in large doses for 30 days, did not have a toxic effect, but rather stimulated the live weight gain in mice, possibly due to amino acids and enzymes included in the feed supplement.

Pathological diagnostics revealed that in mice of all groups the larynx, trachea, and esophagus mucous membranes are pale pink, the skin is elastic, the fur is smooth, and subcutaneous tissue is well defined. The stomach contains a small amount of fodder masses; the mucous membrane is of a pale gray color. The mucous membrane of the small intestine is gray-pink, covered with mucus. In the lumen of the colon feces are observed. Internal organs have no signs of pathological changes; have the color, shape, location and texture inherent to healthy organisms.

The difference in the coefficients of the internal organs between the control and experimental animals has no significant differences (Table 3). Therefore, it is possible to talk about the absence of visible damaging effects on the internal organs of white mice.

Table 3. The relative mass of mice internal organs, (mg / 100g body weight)

Organ	Group		
	1 Control group	2 Experimental group	3 Experimental group
Heart	6.56 ± 0.44	6.16 ± 0.31	6.54 ± 0.28
Liver	72.18 ± 2.12	73.26 ± 1.82	71.78 ± 1.16
Kidney	16.62 ± 0.38	17.14 ± 0.28	16.62 ± 0.21

When analyzing the results of research of toxicity of the biologically active feed additive «Peak Antistress» for animals, no symptoms of acute poisoning were found in all experimental animals, there was no lethality. The administration of high doses of a feed supplement is well tolerated by animals. With the introduction of single doses for mice, no changes in the gain in live weight were detected. The Peak Antistress feed additive does not have chronic toxicity to mice and does not cause pathological processes in the internal organs of mice. The results of testing the biologically active feed additive for animals «Peak Antistress» give reason to believe that the toxicity of this feed additive can be classified as unexpressed. The feed additive for animals «Peak Antistress» must be classified according to GOST 12.1.007–76 to hazard class IV (low-hazard substances). The «Peak Antistress» feed additive does not have chronic toxicity and does not cause pathological processes in the internal organs of mice.

The «Peak Antistress» feed additive was used in the maximum tolerated dose of 2.350 g per 1 ton of feed, which corresponds to intake of 25 mg per 1 kg of body weight of lithium carbonate, or to 6–7 mg of lithium ion per 1 kg of body weight per day.

Table 4 presents the content of the ionized form of lithium in the organs and tissues of chickens of the experimental group and control group.

Table 4. The content of lithium ion in cooked meat, minced meat and by-products

Name	The lithium content, mg / 100 g	
	Experimental group	Control group
White meat	0.418	0.198
Red meat	0.452	0.106
Minced meat	0.376	0.106
Skin	0.271	0.125
Heart	0.352	0.106
Liver	0.340	0.132
Head	0.218	0.130

Conclusion

In result of research it was found that the introduction of the «Peak Antistress» feed additive in amount of 2.350 g per 1 ton of feed for broiler chickens (ionized lithium concentration is 66 mg per 1 kg of feed) allows increasing the lithium content in cooked meat, minced meat and by-products in comparison with product samples of the experimental group. Thus the lithium content in boiled white meat is 0.418 mg / 100 g, which is 211% higher than the control sample; the lithium content in boiled red meat is 0.452 mg / 100 g, which is 426.4% higher than the control sample. Similar results were obtained in determining the lithium content in the skin, heart, liver and head of poultry. Therefore when using 300 g of boiled meat fortified with lithium given in the process of broiler chickens cramming, it provides the recommended daily consumption amount of the specified trace element. The obtained data allow using of raw meat and by-products for the production of lithium fortified food products.

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Original scientific paper

A STUDY ON AN EFFECT OF THE GREEN TEA EXTRACT ON QUALITY AND SHELF LIFE OF ANIMAL FATS DURING STORAGE

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Key words: *antioxidants, fat storage, fat oxidation*

Abstract

An analysis of an effect of the green tea extract on quality and shelf life of animal fats is presented. It is shown that the rate and depth of fat hydrolysis depend on a storage temperature. The higher the storage temperature, the higher the rate of fat hydrolysis and, consequently, the acid value. During storage for more than 3 days at any temperature, fats (except mutton fat) begin to change their properties. Mutton fat shows the first signs of spoilage (an increase in the acid value of more than 2.2 mg KOH, MAC ND) after 10 days of storage. An insignificant variation in the peroxide value of all tested fats during 10 days of storage, which was within the range of MAC, was established. After 10 days of storage, the rate of formation of peroxides and hydroperoxides rose sharply, which was confirmed by the peroxide value of these fats. Addition of antioxidants of the green tea extract in an amount of 10 g per 100 kg fat ensured appropriate storage of all fat types upon storage conditions that corresponded to the normative and technical documentation.

Introduction

According to the state policy of the Russian Federation in the field of healthy nutrition of the population for the period of up to 2020, the most important task is the development of production of foods that facilitate maintenance and strengthening of health of different population groups [1].

The unfavorable ecological situation and nutrition provoke oxidative processes in the human body, which cause cell dysfunction and an increase in cardiovascular, oncological and other chronic diseases. To improve population health, it is necessary to manufacture products, which composition includes natural ingredients with antioxidant properties [2,3].

The topicality of this problem is determined by fluctuations on the market: an increase or decrease in consumer demand, a necessity to transport products over large distances, weather conditions are the main factors that require taking appropriate measures that would guarantee high commercial quality of melted fats.

The production technology for animal fats based on melting includes their dehydration. Therefore, they contain in the final form not more than 0.2–0.3% of moisture, which facilitates an increase in their storage stability. At the same time, edible fats are prone to changes (rancidification and tallowiness) under unsatisfactory storage conditions [3,4].

Recently, a trend towards a pronounced growth in the use of certain fats for improving foods, consumer properties and the nutritional value is observed. It is this direction that is most promising for the development of the Russian market of animal fats.

It is known that most unstable during storage is pork fat, which upon the contact with air oxygen and under an effect of light is subjected to oxidative changes. As a result of chain destructive reactions, oxidation products (hydroperoxides, aldehydes and ketones, dibasic fatty acids) accumulate in fat. A consequence of this are unpleasant odor and taste, as well as color changes [5,6].

The use of inhibitors of oxidative spoilage allows retardation of these negative processes and, thereby, prevention of product spoilage. The main requirements for their use are safety, availability, low cost, simplicity of using, absence of odor and taste, inhibition effectiveness. Inhibitors from natural raw materials are preferable. We propose to use bioflavonoids with the antioxidant properties in the production process as an alternative [7,8].

The aim of the research was to study an effect of antioxidants of the green tea extract on physico-chemical characteristics of animal fats during storage.

Materials and methods

The objects of the research were pork, beef, mutton and goose fats.

Measurement of moisture content

The method is based on drying a fat specimen to a constant weight.

Work procedure. Fat (2–3 g) is put into an empty weighing container preliminarily dried to a constant weight, weighed with an accuracy of 0.0002, placed into a drying oven and dried at a temperature of 100–105 °C. The first weighing is carried out after 1 hour of drying, the following ones after 30 min. of drying. The weighing container is cooled in a desiccator for 20–25 min.

The moisture content X (%) is calculated by the equation:

$$X = \frac{(M_1 - M_2)}{M_0} \cdot 100,$$

where

M_1 is the weight of the weighing container with fat before drying, g;

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M_2 is the weight of the weighing container with fat after drying, g;
M_0 is the fat weight, g.

Methodical note

Considering that fat oxidation is possible, the lowest weight is taken into account in drying.

Determination of the acid value

The acid value characterizes the depth of hydrolytic decomposition of fats and is an indicator of oxidative spoilage in investigation of stored melted fat along with other more characteristic indices. Cleavage of triglycerides of fatty tissue takes place under the action of lipases catalyzing hydrolysis of ester bonds. The reactions of hydrolytic cleavage are accelerated with an increase in a temperature in the presence of bases, acids. Hydrolysis of fat and the corresponding increase in the acid value can occur at the beginning of the technological process mainly by the enzymatic way and then non-enzymatic hydrolysis of triglycerides is possible at the stage of melting after lipase inactivation [9,10].

Principle of the method

Titration of free fatty acids in the ether/ethanol solution of fat with the alkaline aqueous solution.

Ether serves as a fat solvent and ethanol is used for homogenization of the system formed by the alkaline aqueous solution and fat during titration.

Work procedure

Fat (3–5 g) is weighed in a 250 ml conical flask with an accuracy of 0.01 g. Fat is melted in a water bath and 30–50 ml of the neutralized mixture of ethanol and diethyl ether are added. The content of the flask is agitated. Two or three drops of the indicator (1% phenolphthalein solution) are added to the solution and quick titration is carried out until appearance of the pink color.

The acid value is calculated by the equation:

$$X = \frac{5{,}61 \cdot V \cdot K}{M},$$

where

5.61 is the titer of 0.1 N potassium hydroxide solution, mg/ml;
K is the adjustment coefficient to the alkaline solution;
V is the amount of 0.1 N potassium hydroxide solution used for titration, ml;
M is the fat weight, g.

Methodical notes

In case of fluid turbidity in the flask, 5–10 ml of ether/ethanol mixture are added. If turbidity does not disappear, the flask is slightly heated in a water bath and titration is carried out after cooling.

The neutral ether/ethanol mixture is prepared by mixing one part of 96% ethanol with two parts of diethyl ether, the indicator (phenolphthalein solution 1% in ethanol) is added; after that, it is neutralized with 0.1 N alkaline solution to the slightly pink color.

Determination of the peroxide value

The peroxide value characterizes a degree of fat oxidative spoilage. At the first stages of oxidation of fatty acid esters, hydroperoxides are formed. As a result of decomposition or other transformations of peroxides, intermediate and end products of oxidation emerge: alcohols, aldehydes, ketones, low molecular weight acids, oxyacids and others, many of which take part in appearance of odor and taste of spoiled fat. The oxidation rate is influenced by the nature of fatty acids, presence of catalyzers, natural antioxidants, temperature and light. The oxidation reaction is accelerated by heme pigments.

The delay in raw material processing, high temperature, presence of atmospheric oxygen, contact with metallic equipment, effect of light, inadequate storage conditions stimulate peroxide formation.

The peroxide value is expressed as the number of grams of iodine liberated from potassium iodide in the acidic conditions under an effect of peroxides contained in 100 g of fat (% of iodine) [11,12].

There is a certain dependence between the peroxide value and organoleptic indices of fat as substances that change fat taste and odor appear in parallel with accumulation of peroxides (Table 1). A degree of fat freshness is determined depending on the peroxide value.

Table 1. Dependence of fat freshness on the peroxide value

Fat condition	Peroxide value (% of iodine)
Fresh	Up to 0.03
Fresh, but not storable	0.03 to 0.05
Doubtful freshness	0.06 to 0.1
Spoiled	More than 0.1

Principle of the method

Oxidation of hydroiodic acid with peroxides contained in fat with the following titration of liberated iodine with sodium thiosulphate.

Work procedure

A specimen of fat (about 1 g) is weighed in a stoppered conical flask with an accuracy of 0.0002 g. Fat is melted in a water bath. Ten milliliters of chloroform is poured into the flask (along the wall, washing fat particles) from a cylinder; after that, 10 ml of glacial acetic acid and, then, 1 ml of the freshly prepared saturated solution of potassium iodide are added.

The flask is closed with a stopper, the flask content is thoroughly mixed and held in a dark place for 5 min. Then, 100 ml of distilled water and 1 ml of 1% starch solution are added to the flask and liberated iodine is titrated with 0.01 N solution of sodium thiosulphate until disappearance of the blue color.

The control test (without fat) is carried out in parallel.

The peroxide value of fat X (% of iodine) is calculated by the equation:

$$X = \frac{0{,}00127 \cdot K \cdot (V - V_1) \cdot 100}{M_0},$$

where

0.00127 is the amount of iodine that is equivalent to 1 ml of the 0.01 N solution of sodium thiosulphate, g;

K is the adjustment coefficient to the titer of 0.01 N solution of sodium thiosulphate;

V is the amount of 0.01 N solution of sodium thiosulphate used for titration of the test solution, ml;

V_1 is the amount of 0.01 N solution of sodium thiosulphate used for titration of the control solution, ml;

M is the fat weight, g.

Results and discussion

Various transformations occur under the influence of biological or physico-chemical factors during processing and storage of fatty tissue from slaughter animals or fats extracted from it. The contact of meat fatty tissue with air oxygen, water, microorganisms, metals causes physico-chemical and biological processes that change properties of fatty raw materials and meat tissues. The intensity of changes depends both on raw material properties and storage conditions [13]. Oxidative and hydrolytic processes can cause fat spoilage (Figure 1).

As a result, the fat chemical composition changes, the organoleptic indices and nutritional value decline. The processes of hydrolysis and oxidation often occur simultaneously enhancing changes in fat.

A degree of fat spoilage is analyzed not only by the organoleptic, but also by different chemical methods. The results of analyses are usually characterized by arbitrary units — the acid value, peroxide value and other values (GOST R51487–99). Hydrolytic spoilage of fats is characterized by accumulation of free fatty acids. This can be a consequence of autolysis and a result of the action of other factors: acids, alkali, metal oxides and other inorganic catalyzers, as well as microbial enzymes [14].

The hydrolytic decomposition of triglycerides under the action of tissue lipases is observed; as a result, accumulation of free fatty acids expressed in an increase in the acid value of fat is noticed, which is undesirable for fat quality characteristics. The acid value is low and not higher than 0.05–0.2 in fresh fatty tissue just taken from a carcass.

The rate and depth of fat hydrolysis depend on a storage temperature (Figure 2, Figure 3, Figure 4, Figure 5, Figure 6). The higher a storage temperature, the higher a rate of fat hydrolysis and, consequently, the acid value.

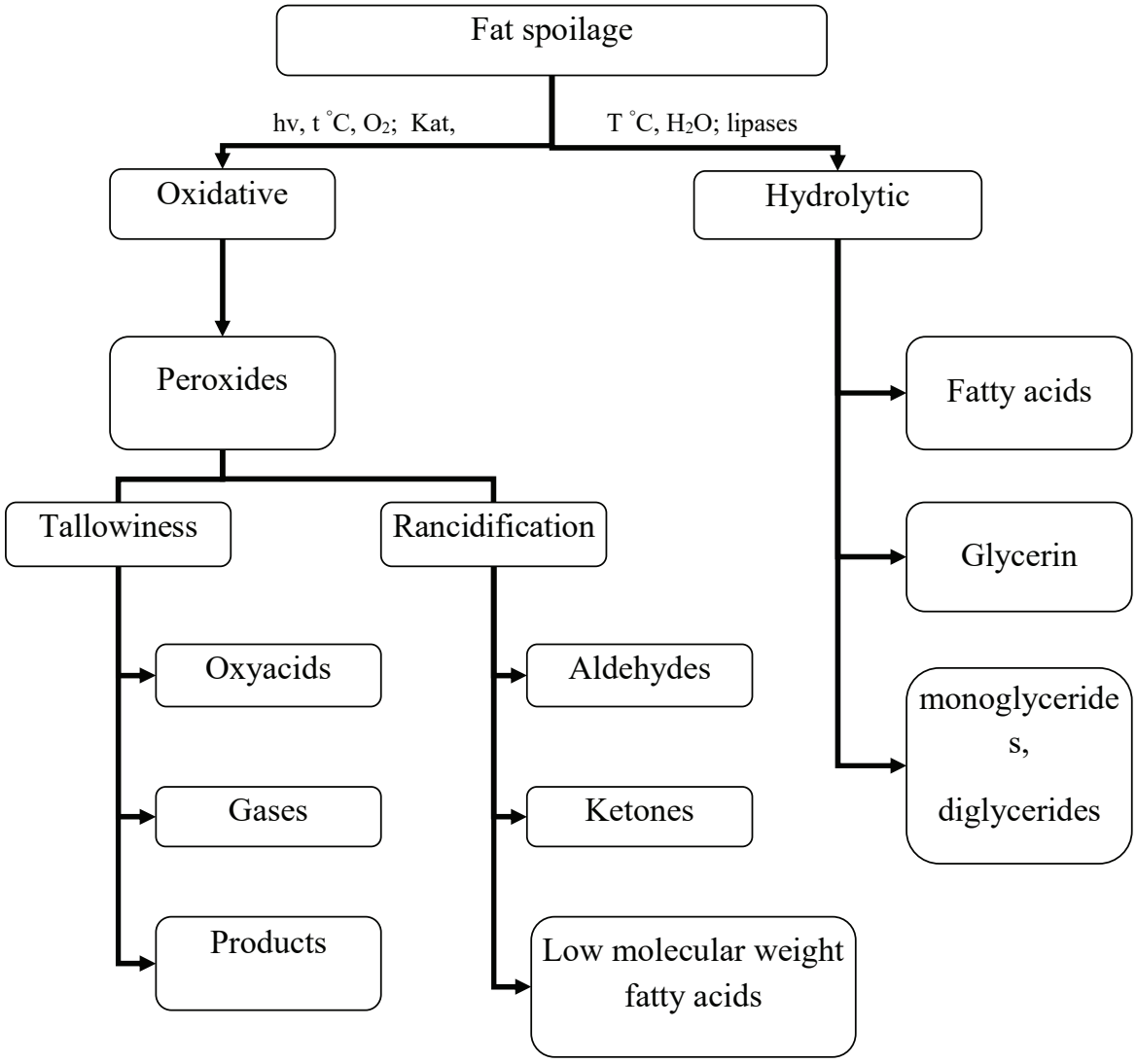

Figure 1. The scheme of fat spoilage

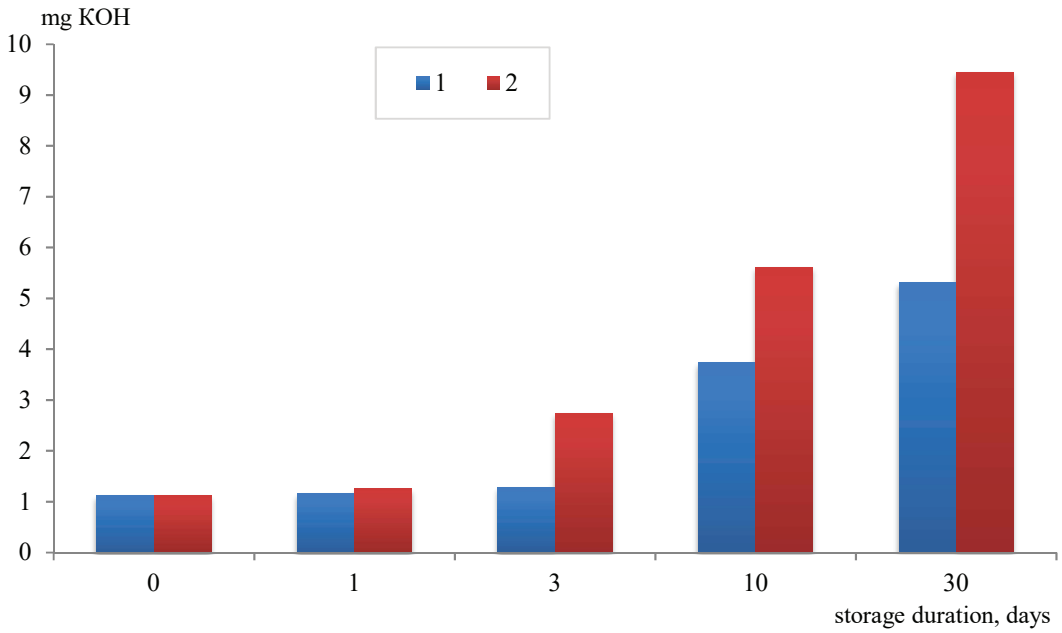

Figure 2. Changes in the acid value of pork backfat during storage at a temperature: 1 at 4 °C; 2 at 20 °C

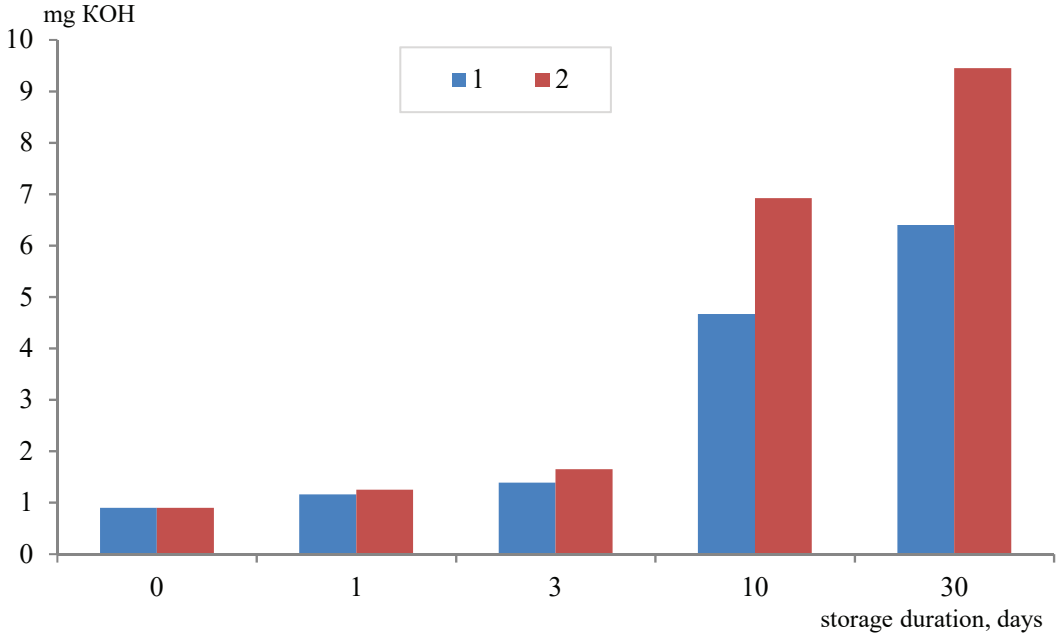

Figure 3. Changes in the acid value of pork fat from flank during storage at a temperature: 1 at 4 °C; 2 at 20 °C

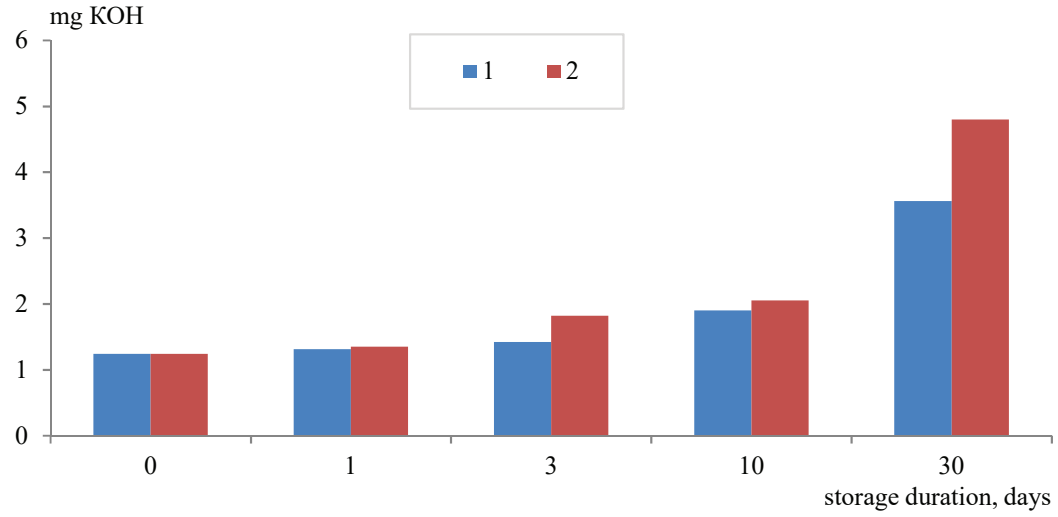

Figure 4. Changes in the acid value of mutton fat during storage at a temperature: 1 at 4 °C; 2 at 20 °C

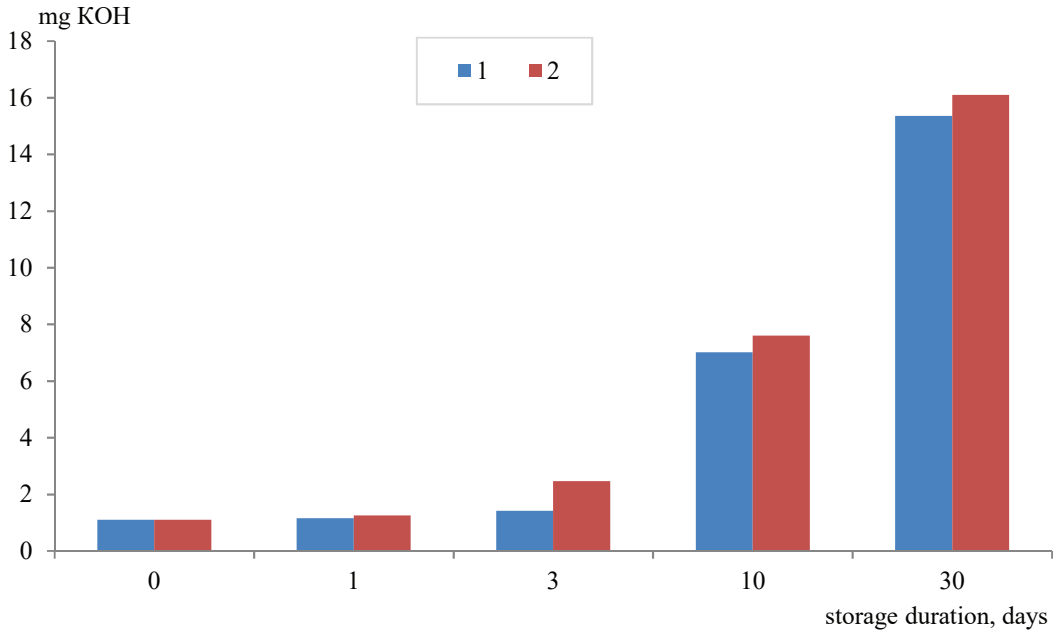

Figure 5. Changes in the acid value of goose fat during storage at a temperature: 1 at 4 °C; 2 at 20 °C

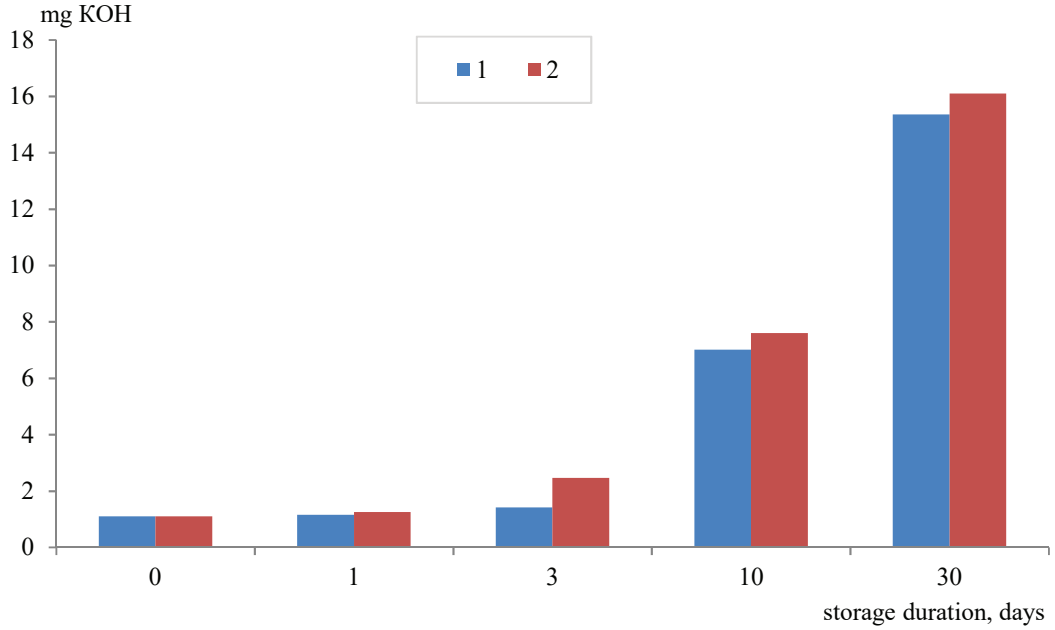

Figure 6. Changes in the acid value of beef fat during storage at a temperature: 1 at 4 °C; 2 at 20 °C

The results of the investigations showed that a temperature had a different effect on transformations of different types of fat. For example, changes in the acid value of goose and mutton fat during one month at a storage temperature of 4 °C and 20 °C differed only by 5%. Therefore, these types of fat can be recommended for the use and storage in warm regions of the country.

Pork backfat and beef fat showed strong dependence on a temperature during storage. Maximum difference was 15%, which suggests a strict adherence to the temperature regimes during storage. Pork fat from flank began to spoil from the third day of storage at a temperature of 20 °C with increased difference in the acid value of up to 30% by one month of storage. Thus, it is not recommended to use this type of fat for production of melted fats without using inhibitors [15].

Analysis of data showed that upon storage for more than 3 days at any temperature, fats (except mutton fat) began to change their properties. Mutton fat showed the first signs of spoilage (an increase in the acid value of more than 2.2. mg KOH, MAC ND) after ten days of storage.

Appearance of a small amount of high molecular weight fatty acids in fat upon hydrolytic decomposition do not cause changes in product taste and odor. In the presence of low molecular weight acids in the composition of triglycerides, hexanoic acid and butyric acid having unpleasant odor and specific taste, which sharply deteriorate organoleptic properties of a product, can be formed upon hydrolysis [16,17].

As a rule, the autolytic cleavage of fat is not observed in melted fats. This is explained by inactivation of lipase contained in fatty tissue, when a temperature reaches 60 °C

during melting. Hydrolytic spoilage of melted fat is possible in the presence of moisture, microbial contamination, incomplete protein denaturation upon melting fat or in the presence of inorganic catalyzers [18].

During storage and processing of fats, their oxidative changes are possible, which can occur with different rates and depths, have different directions depending on natural fat properties and oxidation conditions [10,13].

Oxidation of fats (autooxidation) takes place at low temperatures in the presence of gaseous oxygen.

The beginning and depth of fat oxidation are judged by the peroxide value.

There are no peroxides in fresh fat. At the initial stages of oxidation, chemical and organoleptic indices of fat almost do not change for some time. This period, which has different duration in various fats, is called an induction period. After the end of the induction period, the spoilage of fat begins, which is accompanied with an increase in the peroxide value and changes in fat organoleptic properties.

Occurrence of the induction period is explained by a low number of particles with increased kinetic energy (excited or free radicals) at the beginning of the process [8,12].

The use of antioxidants gives an opportunity to extend the shelf life of food raw materials, semi-products and finished products, protecting them from spoilage caused by oxidation with air oxygen.

Fat oxidation is a complex process, which proceeds by the radical chain mechanism. The duration of the induction period, during which fat spoilage is not observed, depends on the mass fraction of natural (carotenoids, tocopherols, lecithin, vitamins A and K) or artificial (phenol derivatives contained in smoke fume, several natural spices or their extracts, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT)) antioxidants, fat nature and storage conditions [3,19,20].

The mechanism of the antioxidant action consists in their more active interaction with free radicals and air oxygen, due to which radicals are removed from the sphere of the reaction and the chain is broken, thereby, interrupting the autoxidation reaction.

An effect of natural antioxidants, the biologically active complex of the green tea extract, on the acid value under different storage conditions is shown in Figure 7, Figure 8, Figure 9, Figure 10, Figure 11.

It is agreed that a product with the acid value of more than 3.5 mg KOH/g is not storable. As can be seen from the graphs, none of the samples exceeded the maximum allowable level during 30 days. This suggests the effectiveness of using the biologically active complex of antioxidants of the green tea extract in production of fats for food purposes instead of synthetic BHA and BHT.

Then, we examined an effect of the biologically active complex of antioxidants of the green tea extract on the peroxide value (Figure 12, Figure 13, Figure 14).

Analysis of the graphs (Figure 12, Figure 13, Figure 14) shows that addition of antioxidants of the green tea extract in an amount of 10 g per 100 kg fat ensures adequate storage of all fat types under any storage conditions.

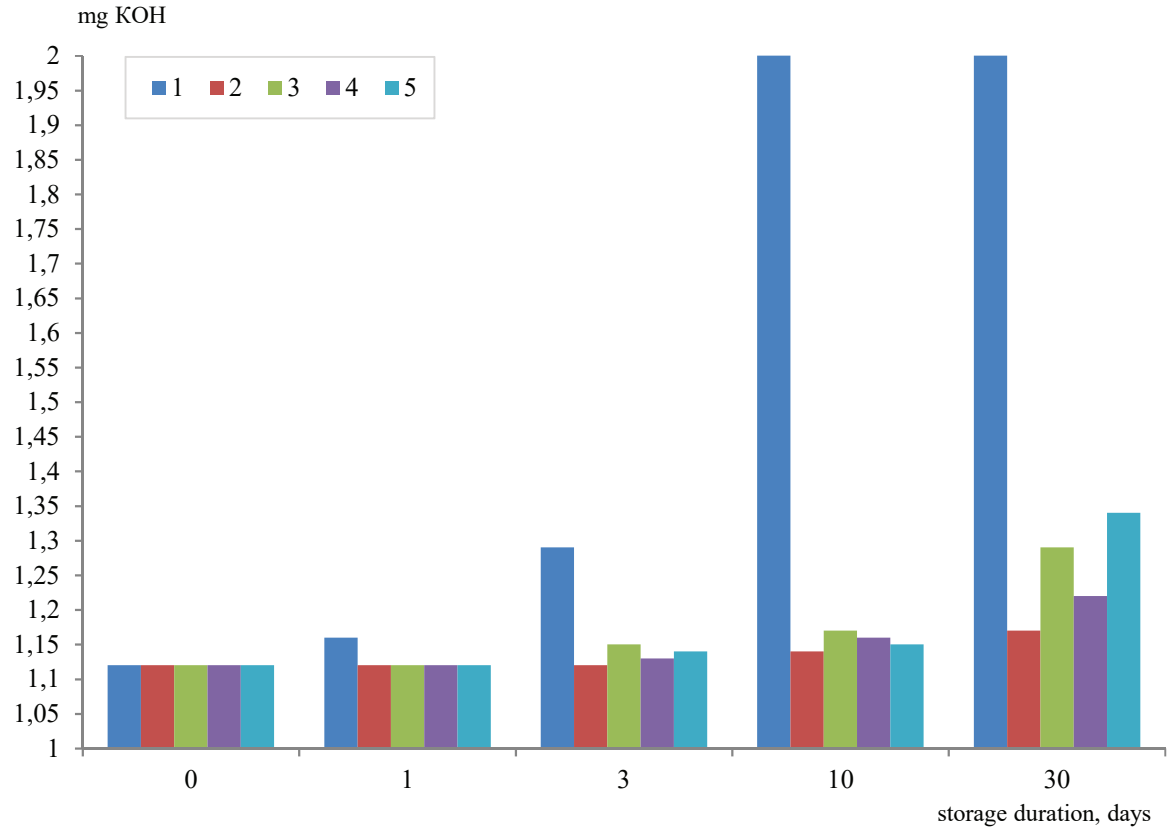

Figure 7. Changes in the acid value in pork backfat under the effect of antioxidants of the green tea extract during storage:
1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

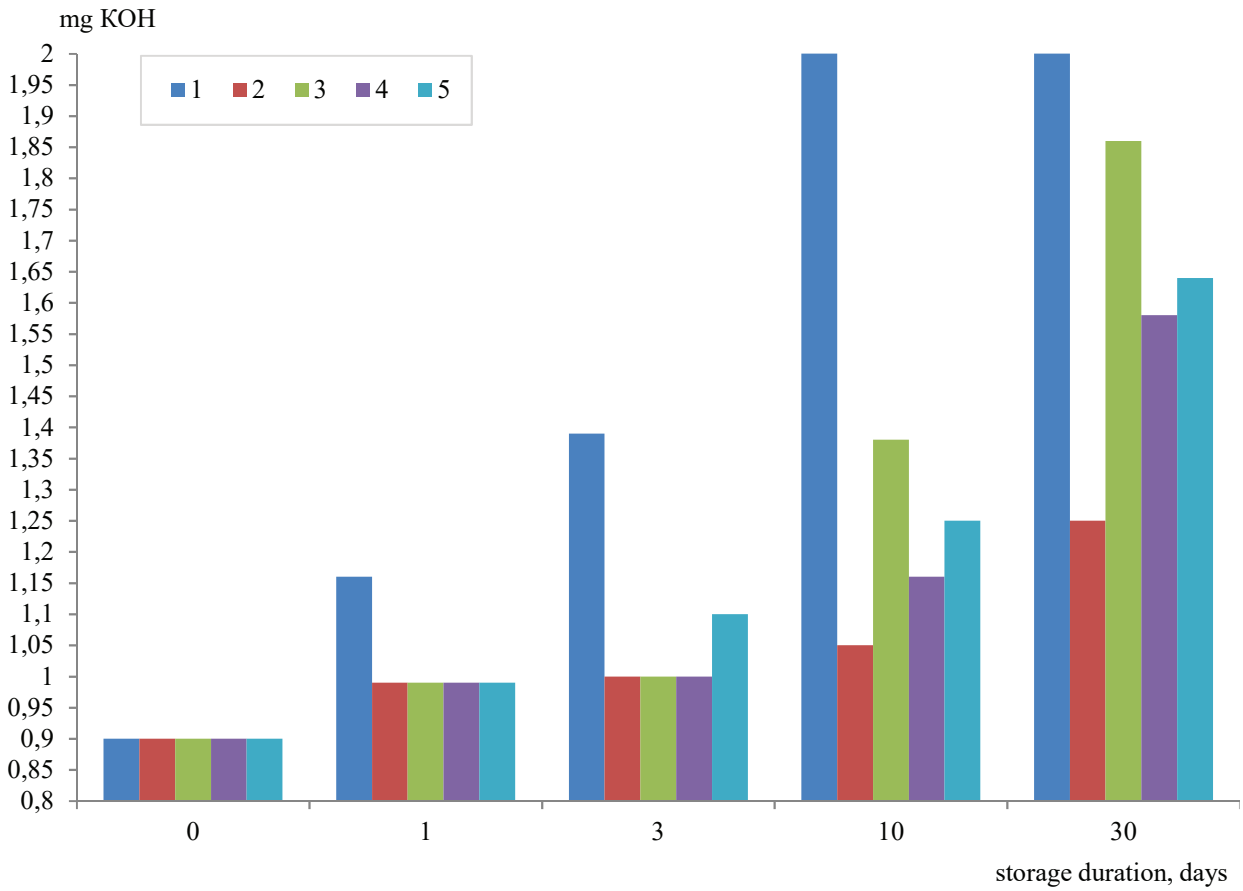

Figure 8. Changes in the acid value in pork fat from flank under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

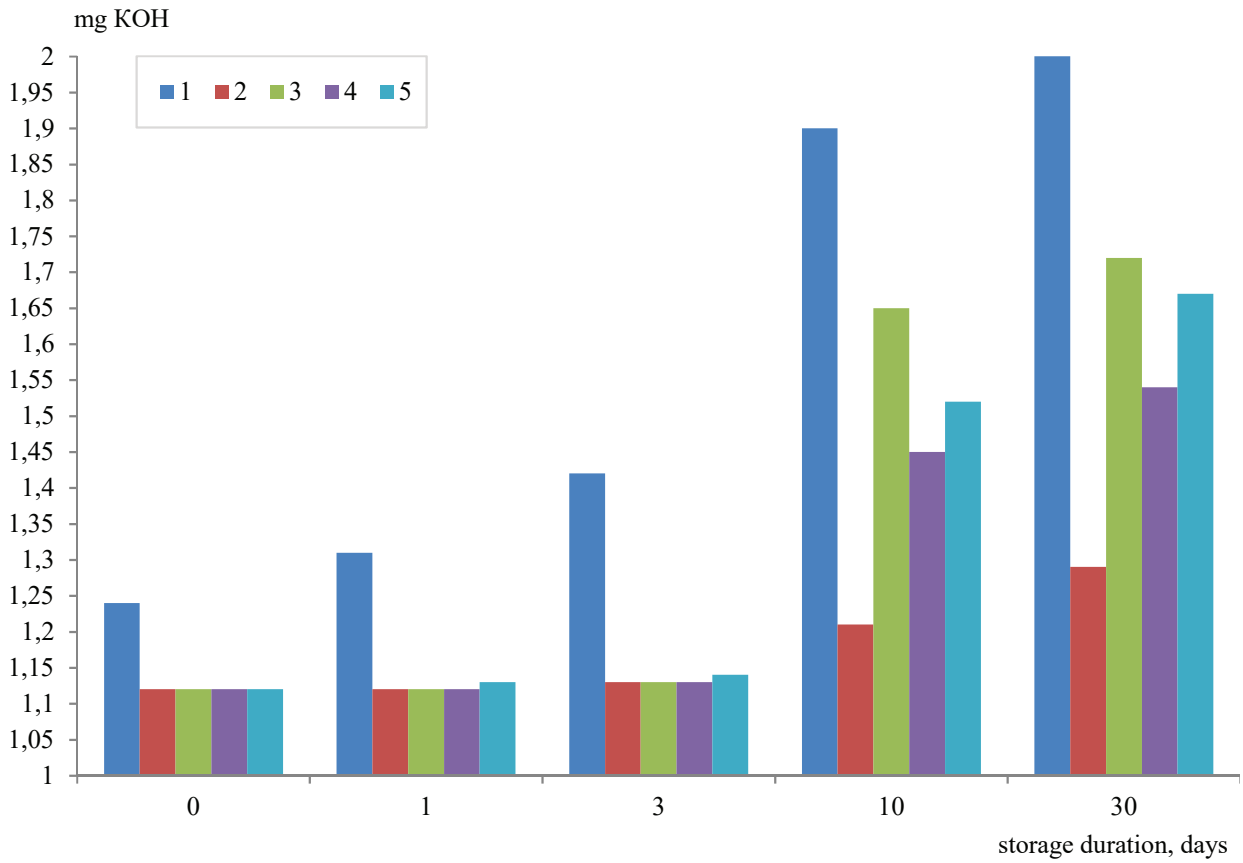

Figure 9. Changes in the acid value in mutton fat under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

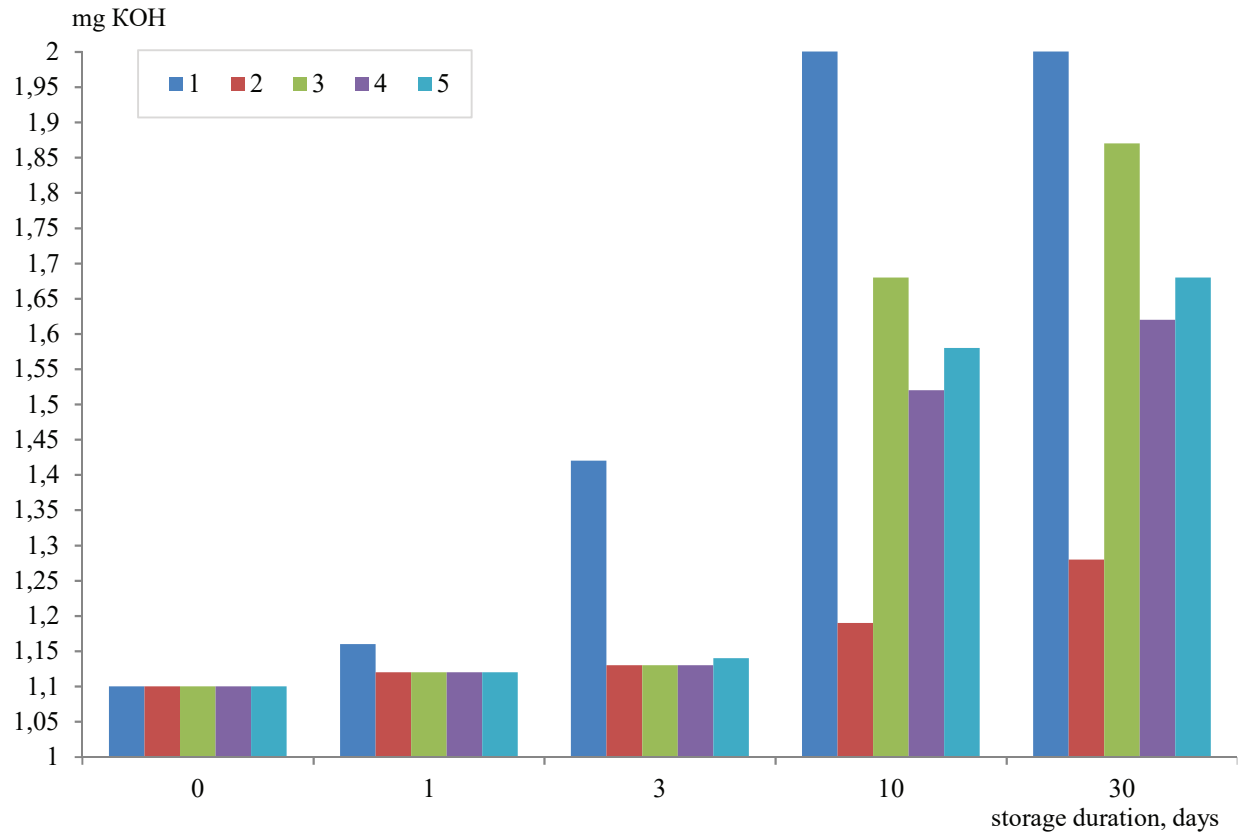

Figure 10. Changes in the acid value in goose fat under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

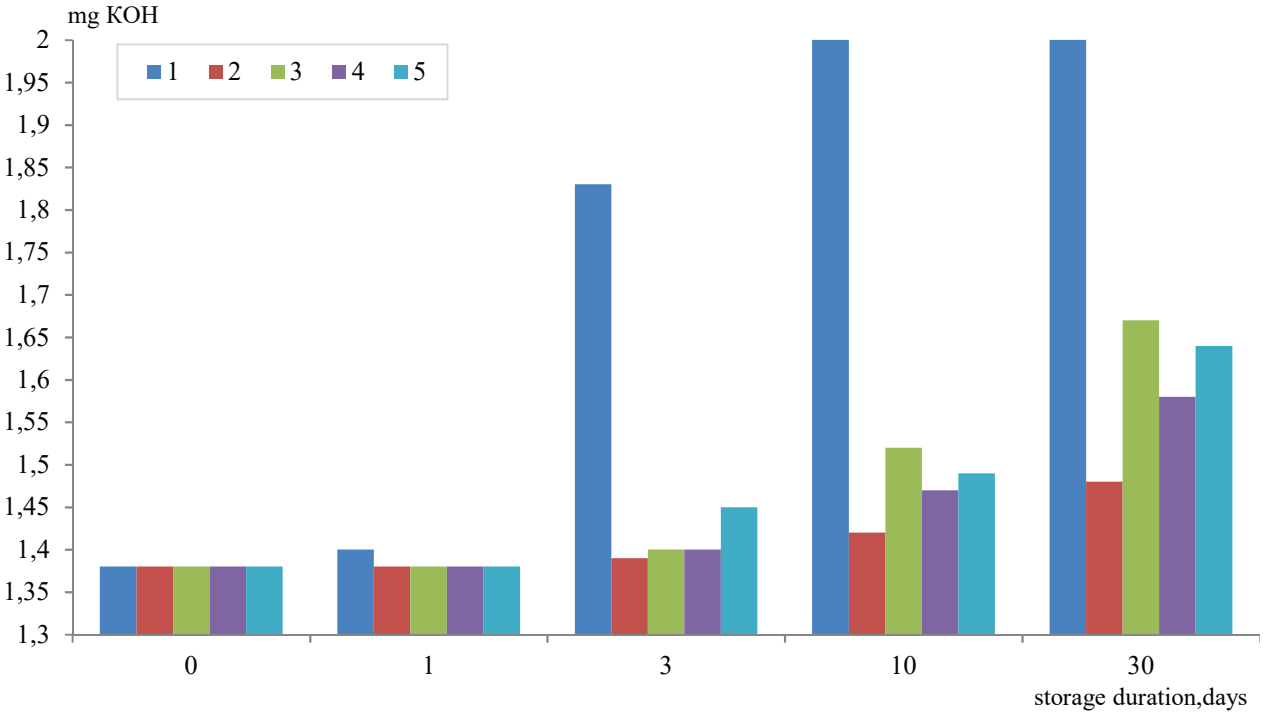

Figure 11. Changes in the acid value in beef fat under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

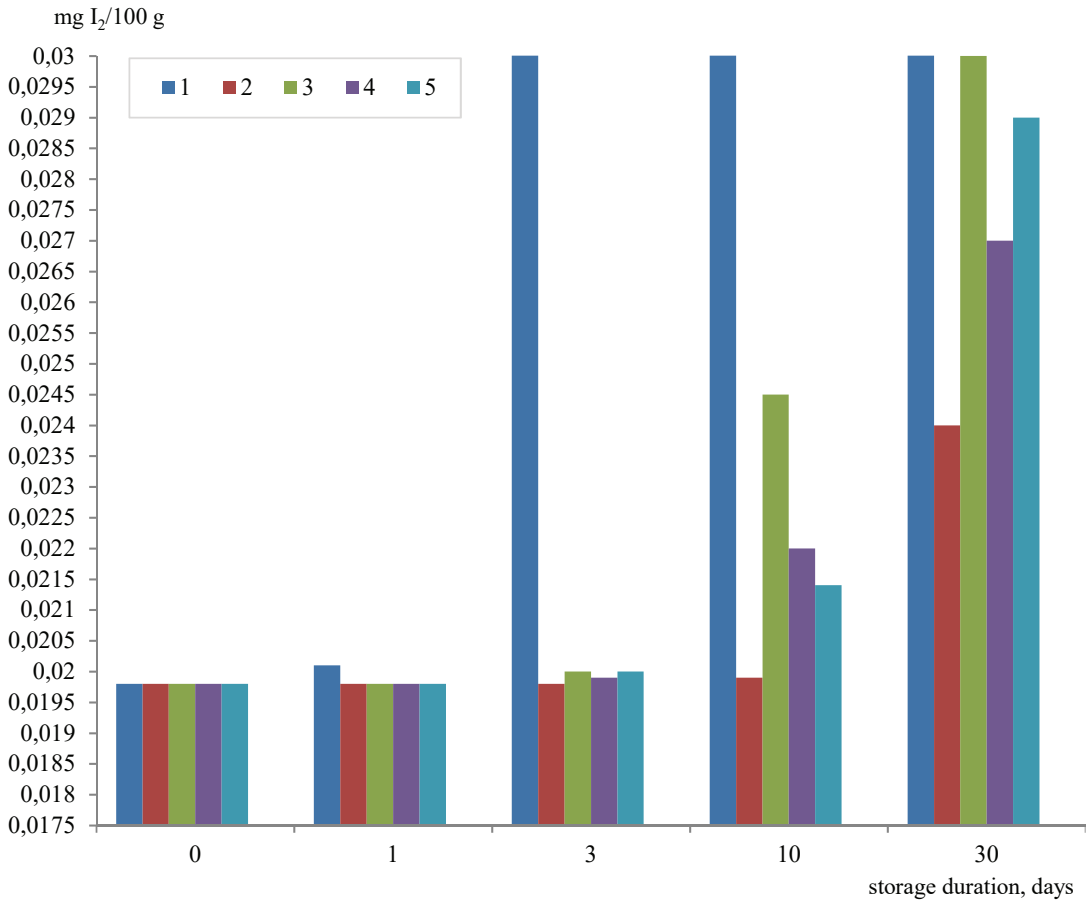

Figure 12. Changes in the peroxide value in pork backfat under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

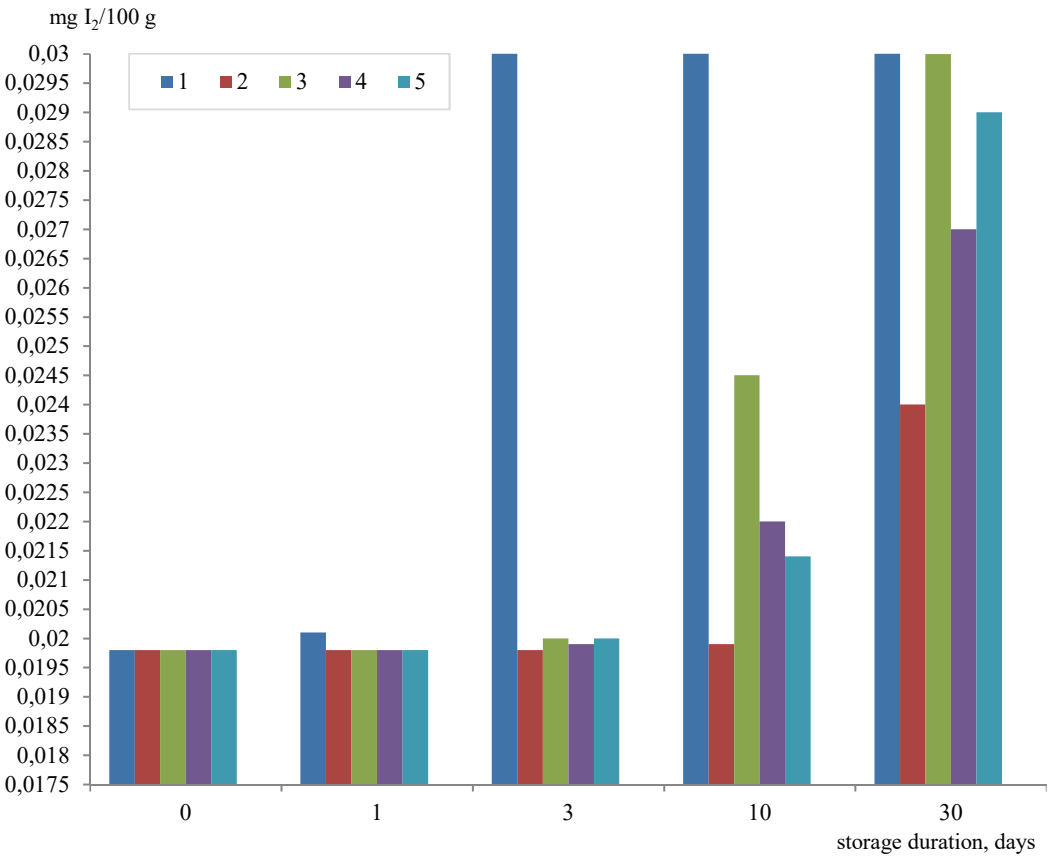

Figure 13. Changes in the peroxide value in pork fat from flank under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

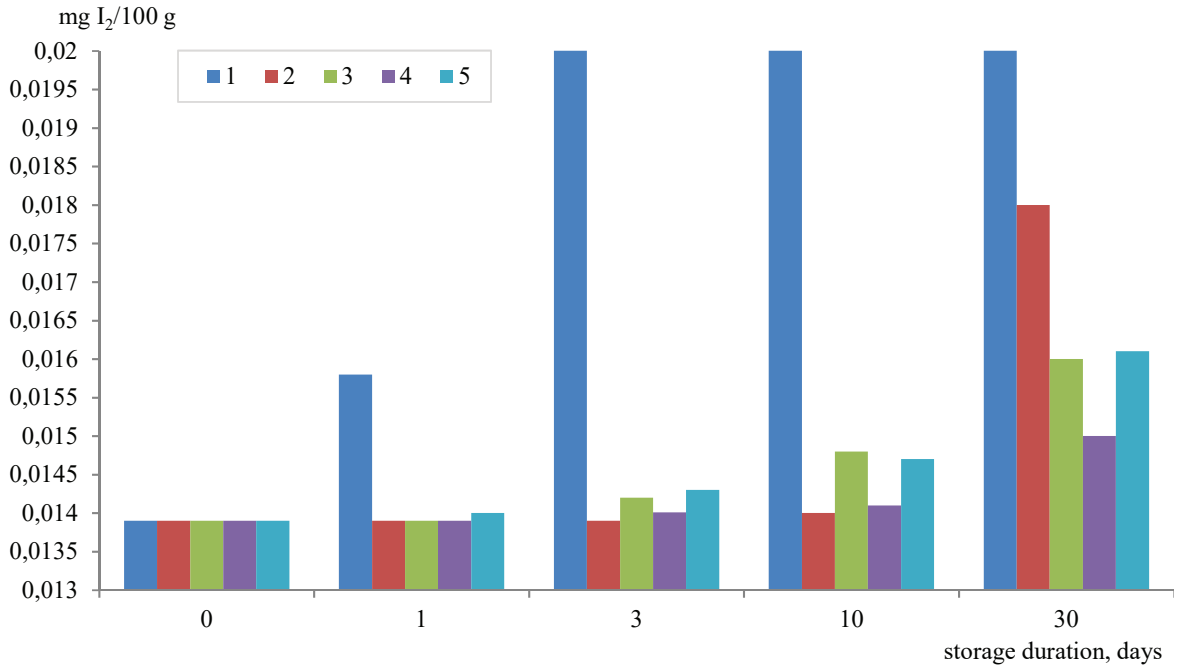

Figure 14. Changes in the peroxide value of mutton fat under the effect of antioxidants of the green tea extract during storage: 1 — control at t = 4 °C; 2 — at t = 4 °C; 3 — at t = 20 °C, under light conditions; 4 — at t = 20 °C, under dark conditions; 5 — at t = 20 °C, under conditions of increased humidity

Conclusion

Analysis of data on the oxidative spoilage indices allowed us to establish that bioflavonoids of the biologically active complex of the green tea extract possessed the antioxidant activity to the full extent, which makes it possible to recommend them for using as additives with the antioxidant action in fat production.

Organoleptic investigations of the fat samples showed that signs of spoilage (slime formation, rancid odor, color changes, darkening and appearance of the greyish tint) were not observed in any sample with addition of flavonoids of the green tea extract during one month of storage.

Therefore, the performed research showed that addition of bioflavonoids of the green tea extract as antioxidants in an amount of 0.01% of fat weight allowed achieving the similar effect as addition of 0.02% BHT. With that, the use of bioflavonoids of the green tea extract did not have a negative effect on fat properties and the human body upon direct consumption.

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