DEVELOPMENT OF A PHYSICAL-MATHEMATICAL MODEL FOR THE PROCESS OF CRYSTALLIZATION OF MEAT SYSTEMS

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1. Introduction

As the rhythm of life is accelerating, the Ukrainian food market faces growing demand for frozen food products. The use of cold in the production of meat and meat products is one of the most effective methods of canning, which makes it possible to maximally retain quality, nutritional and biological value of products over a long time.

Despite significant technical-technological possibilities of the refrigerating treatment, a number of unwanted changes irreversibly occur while freezing due to crystal formation. In order to improve the processes of refrigeration, it is necessary to know their dynamics. As regards the biological raw material of animal origin, there are certain difficulties for the analytical study into these processes. This is due to its heterogeneity in chemical, physical and colloid state, functional-technological properties, which may vary depending on the conditions of treatment, characteristics of breeding animals, etc. The problem is even more complicated when refrigerating multicomponent meat systems.

Therefore, it is a relevant task to obtain a scientifically substantiated system for the estimation of the effect of freezing-defrosting on the properties of meat. This is possible through the use of physical-mathematical models that allow obtaining a complex of information parameters in order to identify and compare thermodynamic changes in meat systems during refrigeration.

2. Literature review and problem statement

Defining the theoretical and practical prerequisites for creating frozen meat products helped form a scientific-practical field related to the manufacturing of frozen semi-finished meat minced products. This research direction aims to ensure convergence of the organizational principles that underlie manufacturing of frozen meat products at meat packing enterprises and in restaurant business.

When freezing meat and storing it at low temperatures, it undergoes a number of physical-chemical changes (crystal formation, freezing out water, structural changes in tissues). The presence of a large amount of water in food products affect the thermal-physical processes during refrigeration treatment and storage of products [1]. For such a multi-component system as the tissue fluid of the meat, this process is quite complex. This is due to the peculiarities of its binding
to other components of products, its large heat capacity, as well as a thermal phase transition during crystallization and evaporation [2].

Research into effect of freezing-defrosting on the properties of biological objects and food systems was addressed in many experimental works and analytical reviews. To substantiate parameters of technological process for obtaining a new product, scientists study the patterns of changes in physical-chemical, functional-technological, microstructural characteristics, in the state and structure of moisture in meat systems during freezing-defrosting. The changes in the muscle tissue of slaughtered animals at freezing are exerted by the breed, age, conditions of conducting the process of freezing-defrosting [3], by the existence of preliminary technological operations (crushing), by the introduction of additional formulation components, by the origin and properties of the non-meat components of formulations [4]. However, such studies are conducted for specific meat systems, they yield relative values and cannot be applied for systems research.

Thermal-physical properties of the product predetermine the character and the rate of the process of heating or cooling within it. A special role is played by the thermal-physical processes during refrigeration treatment of products [5]. They, however, depend on the composition of raw materials, and can vary widely within products of the same kind. These processes in food products are extremely difficult to be modeled mathematically since they include the processes of heat-mass transfer, changes in structural-mechanical properties, physical-chemical and biochemical reactions [6]. Therefore, any technological operations that precede freezing will influence the kinetics of the course of internal transition phenomena.

According to existing models of crystallization in food products, moisture in the product is identified with a true solution, which, during freezing, gradually concentrates up until reaching a eutectic temperature [7]. Although the scientific literature provides much information regarding the influence of freezing-defrosting on meat raw materials, including minced meat, absolute values of physical-chemical, thermal-physical and other indicators vary widely [8]. That is why they cannot be used without experimental determination to define the strategy for ensuring stability of meat frozen systems.

Given that during freezing it is important maximally preserve functional-technological properties and nutritional value of the product, the selected thermodynamic criterion of the process of freezing-defrosting is the degree of its reversibility, which is directly related to a change in specific heat capacity [9]. It is known that the simplest experiment that makes it possible to assess the degree of thermodynamic reversibility of the product during freezing is determining the dynamics of temperature based on the thermograms of the process of freezing-defrosting. At the same time, a mathematical notation of a given process is much more difficult than the experiment itself.

Therefore, in order to identify and compare thermodynamic changes during freezing-defrosting, it is necessary to construct and explore a physical-mathematical model of the crystallization of meat systems. It will become the tool for objective evaluation of the course of physical, physical-chemical, thermal-physical processes during freezing-defrosting of meat systems.

3. The aim and objectives of the study

The aim of present study is to construct a physical-mathematical model of the crystallization of meat systems in order to objectively assess the course of physical-chemical processes in meat systems during freezing-defrosting.

To accomplish the set aim, the following tasks have been set:

1. to establish a relationship between theoretical estimations and experimental data for the effective specific heat capacity of meat systems during freezing-defrosting;
2. to build a physical-mathematical model of the crystallization of meat systems based on the theoretical provisions and principles of nonequilibrium thermodynamics;
3. to devise a method for determining effective specific heat capacity based on the thermograms of freezing-defrosting.

4. Materials and methods of research

We selected as the objects of research the minced meat systems of beef with a different chemical composition. To manufacture minced meat systems, we used chilled beef line with DSTU 6030:2008 whose safety indicators matched Clause 1.1 in “Mandatory minimum list of examining the raw materials, products of animal and plant origin, animal feed raw materials, vitamin preparations, etc., which should be carried out at the state laboratories of veterinary medicine and whose results are the basis for issuing the veterinary certificate”. For the set tasks, the invariability in the chemical composition of the examined samples is achieved and ensured by using the same type of meat raw material within the framework of each experiment.

The technique for obtaining minced meat systems and the method of research into thermal-physical characteristics of minced meat systems are described in paper [10].

Examples of the thermogram curves of samples freezing-defrosting were of the shape shown in Fig. 1.
5. Results of experimental study on the construction of a physical-mathematical model of the crystallization of meat systems

The author showed in [12] that when modeling mathematically the processes of freezing-defrosting one should stop using the known boundary condition by Stefan. It includes the presence of a heat source at the movable contact interface between two temperature fields for the chilled and frozen layer of the product as in reality such a border while freezing the food products does not exist. There are no as well values for true heat capacity of the products, which would not take into consideration the heat of phase transition. Therefore, based on this concept, the basic thermal-physical parameter selected to describe the processes of freezing-defrosting is the specific heat capacity, determined from formula:

\[ c = \frac{dH}{dT}, \]  

where \( c \) is the specific heat capacity, \( J/(kg \cdot K) \); \( dH \) is the change in enthalpy in a given process; \( J \); \( dT \) is the infinitesimal change of temperature in a given process, \( K \).

As is known, specific heat capacity is the additive magnitude, which is why any changes in the composition of meat systems at freezing affect it directly in the linear fashion. In addition, the progress of physical-chemical and biochemical reactions typically has a thermal effect and directly impacts the magnitude of specific heat capacity.

In order to analyze the thermograms of freezing-defrosting, we shall derive a model of the kinetics of a given process taking into account specific heat capacity. We shall use the method of analysis of the kinetics of transfer phenomena in nonequilibrium thermodynamic systems [10] and record the equation of thermal balance for a body of arbitrary shape in the process of convective freezing-defrosting:

\[ R_e \frac{d}{dt}(p\alpha) = -\alpha(t_1 - t_0) - R_e L_w \frac{d}{dt}(p\alpha), \]  

where \( t \) is the temperature averaged by the body’s volume, °C; \( t_1 \) is the body surface temperature, °C; \( t_0 \) is the temperature of the cooling medium, °C; \( R_e \) is the ratio of the body volume to its surface, \( m^3 / m^2 \); \( p \) is the density, \( kg/m^3 \); \( c \) is the specific heat capacity, \( J/(kg \cdot K) \); \( \alpha \) is the coefficient of heat transfer, \( W/(m^2 \cdot K) \); \( L_w \) is the specific heat capacity of the phase transition water–ice, \( L_w = 3.35 \times 10^5 J/kg \); \( w_0 \) is the initial moisture content in parts of the total mass, %; \( \alpha \) is the part of frozen-out (or melted) moisture in relation to the total weight of moisture; \( \tau \) is the current time, s.

We shall write equation (2) in the definitions “effective enthalpy – effective heat capacity”. Assuming that the density of food systems during freezing-defrosting almost does not change:

\[ \rho R_e \frac{d}{dt}H = -\alpha(t_1 - t_0), \]  

where \( H = ct + L_w \alpha \) is the effective enthalpy of the system, \( J/kg \) (which includes the heat of phase transition and other thermal effects).

Thus, based on (1)–(3), effective specific heat capacity of the food product during freezing is written as follows:

\[ C_c(t) = c_o - (c_o - c_w)w_0(1 - \frac{t_c}{t}) + L_w \frac{t_c}{t}, \quad (at \ t < t_c) \]  

and empirical model by Chizhov-Latyshev:

\[ \frac{1.105}{1 + \frac{0.714}{\ln(t + 1 + t_c)}}. \]  

By differentiating the last two equations, we obtain the following expression to calculate effective specific heat capacity at \( t < t_c \) in the Raoul model:

\[ C_c(t) = c_o - (c_o - c_w)w_0 \left[ \frac{1.105}{1 + \frac{0.714}{\ln(t + 1 + t_c)}} \right] \]  

and in the Chizhov-Latyshev model

\[ C_e(t) = c_o - (c_o - c_w)w_0 \left[ \frac{1.105}{1 + \frac{0.714}{\ln(t + 1 + t_c)}} \right] + \frac{0.789}{(t + 1 + t_c)} \frac{L_w \frac{t_c}{t}}{\ln(t + 1 + t_c) + 0.714}. \]

Based on the results of determining effective specific heat capacity for beef meat, we established an essential difference between theoretical estimations based on equations (7), (8) and experimental data (Fig. 2). The characteristic distinction of the experimental data is:

- a wider cryoscopic interval over which we observe a phase transition;
- the offset in a maximum of crystallization rate and cryoscopic temperature toward lower temperatures with a decrease in humidity;
- a lower rate of change in specific heat capacity in the cryoscopic region.

This is caused by a rather rough model of the food product, which follows from the Raoul equation. In the models of
effective specific heat capacity \((7), (8)\), the product is identified with a true solution, which during freezing gradually concentrates until reaching a eutectic temperature.

Fig. 2. Estimated values of specific heat capacity of beef according to classical models \(1, 3\) – Raoul model, \(2, 4\) – Chizhov-Latyshev model at different content of water: \(1, 2\) \((w_0=0.75)\); \(3, 4\) \((w_0=0.22)\).

However, the generally accepted model for food products is the colloidal capillary-porous body (CCPB) whose characteristic feature is the heterogeneity in structural-mechanical properties, chemical composition, binding energy. The moisture in food products is in a dynamic interaction with the disperse phase and can change binding energy both as a result of temperature change and at the expense of denaturation of proteins, conversion of polysaccharides, enzymatic reactions [11]. The complex of these processes cannot be described within the framework of the theory of freezing of true solutions, which is the reason for the above-described differences between theoretical and experimental data.

According to existing theories [13], the process of crystallization in the complex thermodynamic systems, which include meat systems, should be considered as a superposition of several competing processes. For CCPB, these are at minimum two basic processes – freezing out free moisture (main process) and a competing process of increasing binding energy for the bound moisture. The latter manifests itself in the increasing viscosity and gel formation. The above-specified processes are differently dependent on temperature: the rate of freezing out moisture decreases with a decrease in temperature while the speed of the competing process, on the contrary, increases. Graphically it is shown in Fig. 3.

Based on a given physical model, we propose an empirical model for the rate of crystallization in the form of a product of two exponents:

\[
\frac{d\omega}{dt} = A \cdot e^{-k_1 t} \cdot e^{-\frac{t}{k_2}},
\]

where \(A, k_1, k_2\) are the empirical constants; \(k_1\) sets the rate of freezing out free moisture; \(k_2\) is the speed of moisture binding; \(t\) is the temperature (modulo), °C.

Considering expression (9) for the rate of crystallization, effective specific heat capacity at freezing will be recorded in the following form:

\[
C_e(t) = e_0 - (e_0 - e)w_0(1-e^{-kt}) + L_e w_p A \cdot e^{-k_2 \cdot \frac{t}{k_2}} (at t < t_*).
\]

The proposed model of temperature dependence of the effective specific heat capacity is much closer to reflecting the experimental character of the curves, shown for example in [14], than the classic Raoul and Chizhov-Latyshev models.

It is easy to derive characteristic points from equation (10): location of the maximum of crystallization rate (the center of cryoscopic interval of temperatures):

\[
t_* = \frac{1}{\sqrt{k_1 k_2}}
\]

and maximal crystallization rate

\[
\left|\frac{d\omega}{dt}\right|_{max} = A \cdot \exp\left(-\frac{2k}{\sqrt{k_1 k_2}}\right).
\]

Substituting equation (12) into equation (10), we shall find the maximum effective specific heat capacity during freezing

\[
C_{max} = e_0 - (e_0 - e)w_0\left(1-e^{-\frac{b}{k_2}}\right) + L_e w_p A \cdot e^{-\frac{2k}{k_2}}.
\]

Based on the proposed model of the crystallization of meat systems, we developed a method for determining effective specific heat capacity by the thermograms of freezing-defrosting.

In accordance with the definition of specific heat capacity (1), we obtain an expression for determining effective specific heat capacity of the system:

\[
C_e(t) = -k \frac{d}{dt} \int_{t_0}^{t_*} \left(t - t_*\right)dt.
\]

where coefficient \(k\) is derived from equation:

\[
k = a/(R_0 \rho),
\]

where \(a\) is the heat transfer coefficient, \(W/(m^2 \cdot K)\); \(R_0\) is the ratio of the volume of the sample to the area of its surface, \(m\); \(\rho\) is the density of the sample, \(kg/m^3\).

We shall write down equation (14) in finite differences taking into consideration the convenience of processing experimental thermograms, because the temperature of the samples is measured with a specific discreteness (for the experimental installation, \(\Delta t=60\ s\):
\[ C_s(t_j) = \frac{\Delta C}{t_{j,\text{air}} - t_j} (t_j - t_{\text{air}} - t_j). \]

where \( t_j \) is the value of the mean current temperature of the sample, \(^\circ\text{C}; t_{j,\text{air}} \) is the value of the current temperature of the sample’s surface, \(^\circ\text{C}; t_{\text{air}} \) is the value of the current ambient temperature (air temperature in the chamber), \(^\circ\text{C}; \Delta t \) is the discreteness in temperature measurement, s.

The discrete dependences \( C_s(t_j) \), obtained in this way, are approximated using standard procedures of the software Mathcad. The magnitude of coefficient \( k \) is determined either using an estimation method (which employs standard formulae for the calculation of coefficient of heat transfer \( a \) and measured magnitudes of RV and \( r \) for each sample), or experimentally, based on reference sample with known thermal-physical characteristics.

Fig. 4 shows a standard experimental chart for the thermogram of freezing, Fig. 5 – a plot of effective specific heat capacity and its approximation by equation (10).

Information parameters, which were obtained based on the temperature dependence of effective specific heat capacity, are (Fig. 6):
- \( t_{\text{cr,max}} \) – temperature of maximum rate of crystal formation (melting), \(^\circ\text{C}; \)
- \( \Delta T_{\text{cr}} \) – cryoscopic interval of temperatures, \(^\circ\text{C}; \)
- \( \Delta H_{\text{cr}} \) – specific heat capacity of phase transition in a cryoscopic interval of temperatures, J/K;
- \( \Delta \omega \) – share of moisture, which changes its aggregate state in a cryoscopic interval of temperatures (the amount of free frozen-out or melted moisture).

The width of peak at the foot defines a cryoscopic interval of temperatures, in which free moisture is frozen out. The area under the peak in the phase transition defines specific heat of the phase transition in a cryoscopic interval of temperatures.

Considered that a change in enthalpy, caused by phase transition, is equal to:

\[ \Delta H_{\text{cr}} = L_{\text{w}} \Delta \omega \cdot W_{\text{w}}, \]  

it is possible to calculate the share of moisture, which changes its aggregate state in a cryoscopic interval of temperatures.

A change in these information parameters for effective specific heat capacity during freezing-defrosting is the criterion of reversibility of the process of refrigeration.

Fig. 6. Information parameters for temperature dependence of the effective specific heat capacity

6. Discussion of results of the study of a new model for the crystallization of meat systems

The research conducted allowed us to develop and implement a physical-mathematical model for the crystallization of meat systems. A substantial distinguishing feature of the proposed model is that the meat system is regarded as a colloidal capillary-porous body. At the same time, existing models of crystallization in food products identify moisture in the product with a true solution, which, during freezing, gradually concentrates until reaching a eutectic temperature.
out moisture decreases with a decrease in temperature while the rate of the competing process, on the contrary, increases.

Based on this physical model of crystallization, we propose an empirical mathematical model for the rate of crystallization in the form of a product of two exponents, one of which sets the speed of freezing out free moisture with another one assigning the rate of moisture binding.

Based on these concepts, we obtained a dependence of the effective specific heat capacity of meat systems on temperature, and proposed the method for determining it applying experimental thermograms. Processing of the experimental results showed that the model proposed more adequately reflects the actual character of effective specific heat capacity of meat systems with different composition and properties than the classic Raoul and Chizhov-Latyshev models.

Practical significance of a given work is in the fact that the proposed model reflects the actual character of dependence of the effective specific heat capacity of meat systems with different composition and properties; its application will make it possible to implement measures for scientific substantiation and ensuring technological stability of the technology for manufacturing meat frozen food products.

The study conducted became the basis for the scientific substantiation of the technology of semi-finished frozen minced meat products for the criterion of reversibility.

References

7. Conclusions

1. We have established a substantial difference between theoretical estimations and experimental data for the effective specific heat capacity of meat systems. We have proven that the complex of processes that occur during freezing-defrosting of meat systems cannot be described within the framework of the theory of freezing out true solutions.
2. We have developed the physical-mathematical model of the process of crystallization of meat systems, according to which the process of crystallization is regarded as the superimposition of two processes: freezing out free moisture (basic process) and a competing process for increasing binding energy for the bound moisture.
3. We have developed a method for determining the effective specific heat capacity based on the thermograms for freezing-defrosting and a complex of information parameters that allow for the detection and comparison of thermodynamic changes in meat systems during refrigeration. Such information parameters include in our opinion: temperature of maximal rate of crystal formation (melting), a cryoscopic interval of temperatures, specific heat of phase transition in a cryoscopic interval of temperatures, the share of moisture, which changes its aggregate state in a cryoscopic interval of temperatures (the amount of free frozen-out or melted moisture).