Розглянуто склад молока як технологічної системи, яка несе значний термодинамічний потенціал. На основі визначених потенціалів здійснено теоретичне моделювання технологій отримання молочних продуктів. Встановлено, що спрямоване технологічне керування кількістю та формами кальцію у системі «молоко» дозволяє створювати технологічні умови, здатні інтенсифікувати як процеси стабілізації молока, так і процеси одержання кисломолочних продуктів

Ключові слова: теоретичне моделювання, термодинамічний потенціал, кальцій іонний, кальцій міцелярний, фазова рівновага, коагуляція, умови стабільності, декальцифікація, сир кисломолочний

Рассмотрен состав молока как технологической системы, которая несет значительный термодинамический потенциал. На основе определенных потенциалов осуществлено теоретическое моделирование технологий получения молочных продуктов. Определено, что направленое технологическое управление количеством и формами кальция в системе «молоко» позволяет создавать технологические условия, способные интенсифицировать как процессы стабилизации молока, так и процессы получения кисломолочных продуктов

Ключевые слова: теоретическое моделирование, термодинамический потенциал, кальций ионный, кальций мицеллярный, фазовое равновесие, коагуляция, условия стабильности, декальцификация, творог

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DEVELOPMENT OF A THEORETICAL MODEL FOR THE INTENSIFICATION OF TECHNOLOGICAL PROCESSES FOR MANUFACTURING DAIRY PRODUCTS

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1. Introduction

One of the ways to meet consumer demand for high quality and healthy food under present conditions implies a combination of traditional technological approaches and the latest scientific-technical achievements. It is relevant for the scientific-practical field related to processing milk into ready and semi-finished food products, which is based on the basic and applied studies in dairy industry.

In a natural form, milk is the system with inherent properties of fluid (density, viscosity) as a solid medium. At the same time, milk is a mixture of many components of organic and inorganic origin, which are in it as separate chemical compounds and structural elements of [1, 2]. This predetermines virtually all basic technological properties of milk – heat resistance, coagulation and coagulation stability, and others [3].

As far as the understanding of importance of milk in human life activity is concerned, there are many conceptual views, but in most cases they come down to the following. First, milk is a physiological liquid; its natural purpose is to provide newborns with nutrients [4]. It is proven that mother's milk contains biologically active substances, has a high nutritional value, possesses immunological and antibacterial properties.

Second, milk is a food product with defined nutrient properties [5]. Given this, milk is used to satisfy physiological needs of the human body in major nutrients, including protein, fats, carbohydrates, mineral substances, and vitamins. The technological process of producing milk as a food product implies that it is exposed to various types of treatment (mechanical, thermal), which to a certain extent corrects its properties. This increases its organoleptic properties, adjusts nutritional and energy value, modifies the chemical composition. However, an increase in the consumer characteristics leads to a simultaneous decrease in its biologically active and immunological properties.

Third, milk is a source raw material for obtaining a wide range of food products during its processing – sour-milk drinks, kefir and yoghurt [6], sour cream, curds, cheese, cream, milk powder [7], products that possess probiotic properties [8], as well as functional dairy products [9]. It is during processing of milk into target products that a variety of techniques are used for receiving technological effects leading to substantial correction of the composition and properties of milk as a technological system [10].

Based on the specified facts, milk in all three cases is a product that is used to achieve certain physiological or technological purposes. However, in the first case, influencing the composition of milk is undesirable and prohibited, while the second and third cases involve permanent implementation of innovations.

At present, there is considerable progress in terms of understanding the fundamental laws that underlie the processing of milk as a raw material. However, despite the existence of numerous models of coagulation processes, the role of calcium for providing colloidal stability of milk as a polydisperse physical-chemical system is not defined clearly and fully.

Therefore, the development of a theoretical model for regulating the colloidal stability of milk and intensifying its processing, which would account for the amount and form of calcium in its composition, is timely and relevant. The relevance of present research is in establishing appropriate dependences and in developing targeted control influences, which would make it possible to create technological conditions capable of both ensuring the stability of milk in a technological process and intensifying the processes of obtaining sour-milk products.

2. Literature review and problem statement

Despite the intensive development and implementation of innovative technological solutions in the dairy industry, processing of milk as a raw material, with obtaining a wide range of sour-milk products, is carried out employing classic technologies. In this case, most technologies are not reversible in terms of changing the colloidal state of the raw material. This requires maximum level of control over parameters of the technological process related to the starting level of quality of the raw materials [11].

Given this, modeling of the technological processes for manufacturing dairy products becomes a relevant issue, resolving which would minimize technological risks and would make it possible to harness the resource potential of milk in full.

The main difficulty in the process of modeling a colloidal state and its possible changes is in that the system "milk" comprises many components [12] with a simultaneous existence of several phases [13]. In the scientific literature [14, 15], there are indications that the system "milk", as a complex polydisperse system, comprises three phases (emulsion, colloid, equilibrium). These inter-phase equilibria in turn affect the equilibria that acting within each separate phase (Fig. 1.) It should be noted that stability of the system "milk" as the whole system is not always possible to ensure through the stability of one of the structural elements. This is due to the fact that the impact of separate components on the system as a whole is not always clear and predictable [16].

Interactions between separate phases and within them predetermine complex structure of milk and its resistance to chemical, physical and biological impacts during technological processing of milk in the production of food products. In the opinion of authors of [17], the most sensitive to technological and biological influences are the colloidal and molecular disperse phases. In this case, even a slight change in their qualitative composition can cause a probability of destabilization in the phases and destruction of the polydisperse system, that is the separation of milk into separate phases (solid and liquid).

Given this, the main directions of modeling are the creation of mathematical models for coagulation processes in the system "milk", which are accompanied by a decrease in stability and the emergence of a new phase [18].

Based on the theoretical analysis of thermodynamic state of the system of "milk", the following occurs. In line with the Gibbs phase rule, formation of a new phase is possible in two cases:

– under condition of the external influence of temperature and/or pressure;

– under condition of the addition of a new phase or a chemical substance that are able to form a new phase.

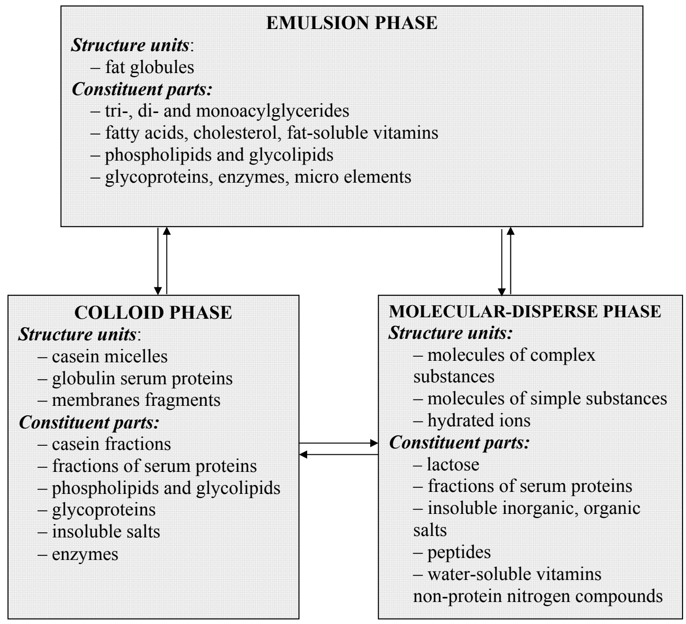

Fig. 1. Model of equilibrium state and possible interactions between separate phases in the system "milk"

Given that the first case is not effective for technological reasons, we shall consider the second case. It implies adding a new phase with the specified (predefined, controlled) chemical potential. In this case, it is necessary to immediately assign the kind of phase and the properties. Moreover, the phase equilibrium and the new phase that was created must be technologically stable. We can choose a solid phase as the phase, with a certain geometrical shape, for example, a sphere. Thus, the state of equilibrium, which is regulated, relates to the external and internal surfaces of the sphere. In this case, both on the outside and inside the sphere is in contact with a liquid phase of different chemical composition.

Mathematical modeling of the process of change in the colloidal stability of caseins at the stage of formation of milk clots with the emergence of new phases is based on two methods:

– the Monte Carlo method [19];

– the method of molecular (Brownian) dynamics [20].

Thus, in order to describe the initial stage of coagulation, it was proposed to apply the model of "sticky" rigid spheres described in papers [21, 22]. According to this model, a casein micelle can be represented in the form of a spherical solid particle whose surface is covered with the so-called "hair layer". A "hair layer" is the hydrophilic areas of the polypeptide chains of κ-casein – glycemacropeptide protruding from the surface of the micelle. Under the influence of technological factors (for example, effect of the rennet extract, or accumulation of hydrogen ions), the " hair layer" is destroyed, which leads to interactions between separate micelles. The main advantage of this model is its physical nature, that is, the ability to predict the process based on the structures and properties of the system.

In terms of the model of the surface charge, colloid stability of casein is provided both through Coulomb repulsion and due to steric stabilization. The latter occurs through the formation of a hydrate layer on the surface of micelle, formed in the interaction between water and a glycemacropeptide. In this case, an increase in the negative charge of the micelle is observed, which is formed through the dissociation of functional groups of caseins. It is considered the main cause of the colloidal stabilization of casein. Therefore, in the framework of the proposed model, the main factor, which describes coagulation resistance is the magnitude of charge on the surface of the micelle [23, 24].

Modeling of the structure formation process in the protein systems of milk is addressed in paper [25]. The authors established patterns of influence of the dynamics of losses of colloidal stability in the micellar system "milk" on the rheological properties of modeling gels. The model implies applying the method of molecular (or Brownian) dynamics, in which the motion of molecules is determined by the forces of two types: random (diffusing) and regular interactions. The application of such a model in the system "milk" has a practical importance because it allows predicting the rheological properties of milk clots, which is necessary to receive dairy products with predefined functional characteristics.

However, the mechanism of the calcium ion influence on coagulation processes was not established unambiguously. Researchers [26–28] assume in terms of a model of the combined impact of several specific mechanisms:

– destabilization of surface charges – bound calcium ions reduce the total negative charge of micelles by adsorbing on the surface;

– steric destabilization – bound calcium ions smooth the surface of layer of the adsorbed water;

– flocculation – calcium ions bind phosphoserine residues of protein molecules;

– electrostatic repulsion – the non-bound calcium ions in a double electric layer mask interaction of the type charge-charge.

Given the above, it should be noted that at present, despite the existence of a large number of experimentally confirmed facts and theoretical models, there is no an unambiguous interpretation of the process of colloidal stabilization of the system "milk". This is due, above all, to the multicomponent and extraordinary complex interactions both within a separate phase of the system and between phases.

Thus, there an objective need for the theoretically substantiated models of the stability of the system "milk" at control influence on the object. Accordingly, the development of theoretical modeling and experimental verification of the models for colloid stabilization/destabilization of the system "milk" is of theoretical interest and offers prospects of practical implementation. The implementation of such models will make it possible to correct, to a large degree, parameters of the technological process depending on the quality of the original raw materials, to optimize technological processes, contribute to intensification. The result will mean obtaining ready products with standardized quality indicators, as well as economically substantiated approaches to processing milk employing resource- and energy-saving technologies.

3. The aim and objectives of the study

The aim of present study is to construct a theoretical model for controlled intensified technologies of dairy products, based on the quantitative and qualitative analysis of physical-chemical properties of constituent compounds, specifically calcium.

This will make it possible to implement stabilization principles of the system "milk" as a food product, as well as to develop ways for the intensification of technological processes for manufacturing sour milk products.

To achieve the set aim, the following tasks have been solved:

– to establish dependence between the amount and forms of calcium in milk and its technological purpose;

– to perform mathematical modeling of the colloidal stability of the system "milk" as the basis for predicting the techniques of intensification of technological processes for manufacturing dairy products;

– to verify the adequacy of the developed model in the course of implementation of the technological process for manufacturing fat-free milk with controlled thermal stability;

– to verify the adequacy of the developed model in the course of implementation of the technological process for manufacturing cottage cheese.

4. Materials and methods for studying the system "milk" and cottage cheese

We have investigated the following objects:

– skimmed milk supplied by ATZT "Zmiyiv dairy plant" (Zmiyiv, Ukraine);

– the complex forming agent FD-157 – sodium alginate (AlgNa) (produced by firm Danisco, Denmark); its application is allowed by the central body of executive power in the field of health protection in Ukraine;

– skimmed milk with a different calcium content, which was achieved by the sorption of ionized calcium AlgNa;

– sour-milk cheese derived from skimmed milk at intensification of the technological process.

Solutions of AlgNa were obtained by dispersing the batch of AlgNa in drinking de-aerated and de-mineralized water at a temperature of 18–20 °C for (3–4)·60 s followed by holding for 24·602 s.

4. 1. Theoretical methods of representation of thermodynamic systems

To describe thermodynamic systems, we employed so-called parameters of the state and functions of the state that apply only for the entire system in general because they hold under conditions that occur for all properties of the system [29, 30]. In order to describe nonequilibrium processes thermodynamically, we used the concept of thermodynamic potentials.

4. 2. Methods for studying skimmed milk with a different content and state of calcium

The total content of calcium in the system "milk" was measured by a method of complexometric titration. The method is based on the interaction between calcium and Trilon B in an alkaline environment. The result of this reaction is the transition of calcium from compounds with proteins and phosphorus into a solution. The remaining Trilon B was titrated with a calcium chloride solution [31]. Mass fraction of the ionized calcium in the examined samples was determined using a potentiometric method applying a calcium-selective electrode [32]. Active acidity of the skimmed milk was determined using the pH meter pH-150 MI (made by Measuring Equipment, Russia) equipped with an electrode system for measuring pH.

Thermal stability of food systems was determined by alcohol test. The method is based on the coagulation of milk proteins under the action of ethyl alcohol. The essence of a given method is in the addition of aqueous solution of ethyl alcohol at different concentration (68 %, 70 %, 72 %, 75 %) to the examined samples in equal amounts. In the case when the coagulation of a protein component did not occur, the systems were considered thermally stable.

Active acidity and the ionized calcium content in milk protein clots were determined using techniques similar to those employed in the study of milk. Organoleptic estimation of the samples was carried out by a sensory analysis [33].

Experimental research was performed in the laboratory of rheological studies at Kharkiv State University of Food and Trade (Ukraine).

5. Theoretical modeling of technologies for obtaining dairy products for the amount and state of calcium in the raw materials

Underlying the theoretical model of colloidal stability of milk as a technological system is a scientific hypothesis. It assumes that a controlled change in the enthalpy and entropy factors makes it possible to purposefully regulate state of milk, dairy products and milk mixtures. This would contribute to the intensification of technological processes, to ensuring stable quality indicators of the finished products, to extending the product range.

It should be understood that any potential that might be detected in the system "milk" ("dairy products") is a quasi-determined magnitude. Due to the very complex structure of the system "milk" for colloid composition, the existence of biochemical and enzymatic factors, it is very difficult to capture and retain over time the magnitude of the derived potential in the range of equality (1)–(3):

$$P = \text{const}, \quad (1)$$

$$\frac{dP}{d\tau} = 0, \quad (2)$$

where P is the detected potential.

Under an actual technological multicomponent system "milk", it will always be the sum of i-th potentials.

$$P = \sum P_i. \quad (3)$$

Given that the chosen potential is an additive magnitude within a complex system (3), conditions (1), (2) can be satisfied in many ways in terms of existing chemical compounds and structures. This causes the stability of the system in certain limits of technological operations (temperature, mechanical impact, adding certain fluids and chemical compounds).

At the same time, clearly manifested dynamism of the system "milk" is the reason for changes in properties over time, as well as high sensitivity to separate perturbing external factors. Under practical conditions, this leads to obtaining food products with certain deviations from the declared quality level, even under strictly controlled manufacturing processes. Since the technological process of milk processing is an open system, then there are spontaneously "running" uncontrolled and non-significant processes driven by the external environment at certain stages of the technological process. This is the reason why many technical characteristics of products accept wide deviations from rational parameters of the highest quality. These deviations become more significant when the milk processing time intervals are prolonged. This is especially important for the technological processes of manufacturing dairy products and cheeses.

Thus, it becomes obvious that the controlled intensification of technological processes, and the use of technological techniques, which are capable of retaining the specified thermodynamic or chemical potentials is the essence of stabilization of the quality of milk and dairy products. This is the quintessence for designing modern scientifically grounded technological processes.

For fresh milk, a sufficient condition for stability is the stability of colloidal complexes relative to the formation of new phases. Of many colloidal milk microsystems, the most pronounced susceptibility to destruction will be demonstrated by complexes, which will be clearly sensitive to changes in the thermodynamic equilibrium in milk. Perturbing factors that are most influential while changing the equilibrium is the accumulation of hydrogen ions that is registered through changing pH of the system whose magnitude will depend on the intensity of biochemical transformations of milk hydrocarbonates, as well as lactose.

Moreover, the most sensitive to a change in pH will be complex calcium phosphate salts that are found in milk in the form of a colloidal phase. They form the nuclei of a colloidal particle and, together with a real (ion-molecular) solution, build a complex structure of the micelles. The predicted sensitivity of the salt colloidal phase, compared with protein components, is defined by relatively low molecular masses (M.m. $(CaHPO_4)$n=136.0, M.m. $[Ca(H_2PO_4)_2]$ n=234.02) and buffer capacity as a magnitude of resistance to a change in the properties of a liquid medium (a solvent). Note for comparison that M.m. of casein is in the range of 20,000–100,000 Da.

It is evident from Fig. 2 that stability of the system "milk" is ensured by at least three components, the equilibrium among which can be expressed by four coefficients – k_1, k_2, k_3, k_4.

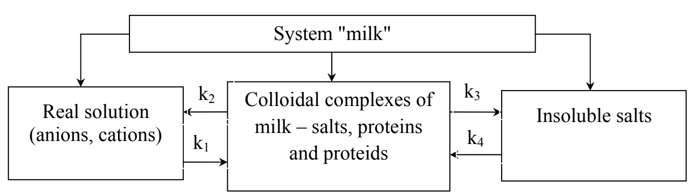

Fig. 2. Block diagram of possible transformations of colloidal complexes of milk in the technological process and during storage

Based on the preconditions for technological stability of milk, which in general is controlled for acidity (16–17 °T, which corresponds to the value of pH of the system in the range of 6.7–6.8), it can be recorded from a colloidal viewpoint as the equality of coefficients (4) and (5). This equality near the equilibrium state describes flow rate of mass exchange, dissociation and (or) transformation of chemical compounds $[k_i] = c^{-1}$. Using these coefficients makes it possible to describe dynamic stability of the system according to block diagram (Fig. 2):

$$k_1 = k_2, \quad (4)$$

$$k_3 = k_4. \quad (5)$$

Understanding that the mass concentration of soluble salts is relatively low allows us to characterize stability of the system “fresh milk” by expression (6):

$$C_{Ca_m} + C_{Ca^{2+}} = 1, \quad (6)$$

where C_{Ca_m} is the mass concentration of calcium-containing salts in the composition of colloids in the system “milk” (relative to the total calcium); $C_{Ca^{2+}}$ is the mass concentration of calcium ions in the system “milk” (relative to the total calcium).

Indeed, such a formal recording of condition of the system “milk” is valid because, based on analytical data for fresh milk (pH=6.6–6.8), the share of C_{Ca_m} accounts for about 90.0–96.0 % by weight (calculated to the total calcium), and the range of calcium ion content $C_{Ca^{2+}}$ is 4.0–10.0 % by weight. It is evident that the condition for absolute thermodynamic equilibrium of fresh milk is:

$$\left.\begin{aligned} C_{Ca_m} &= 1 \\ C_{Ca^{2+}} &\to 0 \end{aligned}\right\} k_1 \gg k_2, \quad (7)$$

since only ionic calcium has the chemical potential and there are no conditions for dissolving calcium-containing colloids in the system “fresh milk” at all. Then:

$$k_1 = 1, \quad (8)$$

$$k_2 = 0. \quad (9)$$

It is evident that in order to achieve colloidal stability of the system “milk” (while ignoring other conditions), that is, to satisfy condition (6), it is appropriate to separate (colloidal isolation) free ions of Ca^{2+} from milk. It is actually possible to predict that the practical implementation of condition (7) will lead to the stabilization of milk properties during storage.

In the course of significant milk acidification (without taking into consideration the nature of a given process) to pH 4.3–4.7, as well as when creating conditions to reduce pH well below these values, the following conditions occur:

$$k_4 \gg k_1, \quad (10)$$

$$k_2 \gg k_1. \quad (11)$$

This factor specifies the maximum (ideally – full) transition of mineral part of the participants of scheme (1) into real solution. It is clear that such an interpretation is general because in the actual process it is necessary to choose a characteristic solvent for different colloidal salts. In this case, the new conditions of thermodynamic equilibrium are observed, which can be described based on the content of Ca^{2+} ions by expression:

$$\mathrm{C}_{Ca^{2+}} \to \max. \quad (12)$$

Considering expression (6), at a complete hydrolysis of mineral complexes, the following expression holds:

$$1 - C_{Ca^{2+}} = 0. \quad (13)$$

Then:

$$k_2 = 1, \quad (14)$$

$$k_1 = 0. \quad (15)$$

In the case of fresh milk, equation (7) corresponds to the maximum magnitude of entropy and chemical passivity of the technological system since the conditional chemical potential of such a system, provided (7) is fulfilled, is almost zero.

The presence of Ca^{2+} ions disrupts chemical stability of the system. And a possible increase in the concentration of these ions under the influence of self-acting potentials, or under the influence of perturbing, or control, factors, can significantly change general properties of milk as a system. In addition, such an effect may lead to the disruption of the colloidal equilibrium, which will be reflected by a change in coefficients $k_1 \ldots k_4$. That is why expression (7) is the main condition for the stability of milk as a colloidal system.

The transition of the system from state (7)–(9) to state (10)–(13), from a chemical point of view, is the chemical reduction reaction with the accumulation of free ions in the form of cations, which can proceed only under condition (16), when:

$$k_4 \cdot k_2 \gg k_3 \cdot k_1. \quad (16)$$

Such processes are thermally-dynamically intensive and occur only in the presence of energy potentials in the system. Such potentials in the system “milk” are inherent to carbohydrates since the hydrolysis of glucose (lactose) to acids releases energy.

Expression (13) is the condition for the thermodynamic stability of dairy products. This is due to the fact that milk acidification improves conditions for the solubility of micellar forms of calcium beyond its ratio to milk proteids or insoluble mineral salts. Certainly, the absolute value of a given expression is a hypothetical magnitude since both the conditions for solubility and the characteristics of a solvent for various colloidal substances of the system “milk” will be of selective character and values. It should be understood that this expression satisfies the condition for a positive entropy gain in sour milk products. Taking into consideration that each separate type of dairy products is characterized by unique organoleptic (for acidity, composition) and physical-chemical (for pH, mineral composition, the degree of hydrocarbonates hydrolysis) characteristics, we can argue about the following. Expression:

$$0 < 1 - C_{Ca^{2+}} < 1 \quad (17)$$

could be accepted as a formal notation of the potential existence of the *i*-th sour milk product.

The given system of formal expressions (6), (7) and (17), in conjunction with technological objectives, can be adopted at the first stage as a basis for predicting (estimation) quality level of a sour milk product. And at the second stage – to determine the conditions and parameters for its stabilization in the technological process.

Together, these three expressions can be regarded as a general phenomenological characteristic of states of the system “milk” in the technological process of its processing into sour milk products. It is obvious that the state of the product described by equation (17) can be obtained through the transformation of the system “milk” (6) using traditional methods of processing or blending the system “milk” (6) with a system that meets the criteria of equation (13) in certain amounts. This means that a sour milk product can be received from fresh milk employing a more intensive technique. For example, by fortifying it with its milk substance (serum), which is described by equation (13) in ratios that enable the formation of state (17). Such a state is unique and characteristic only of a given type of product under condition that one knows characteristics of the product relative to equation (17). This approach will especially be effective for the implementation of the process of obtaining soft cheeses. Adding to fresh milk serum in state (13) would actually change the thermodynamic potential of the system. However, such blending would never affect the quality indicators of the cheese received.

6. Discussion of results of approbation of the theoretical model for control over colloidal stability of the system “milk”

It is very important at the first stage of research to define in a formal form the key role of components in the chain “milk – lactic acid product – serum”. This would make it possible to estimate the thermodynamic potentials of the system, which could be employed in the implementation of fundamentally new technological processes, as well as to ensure stability of the systems “milk” and “dairy products”. This will make it possible:

– to determine conditions for stability of the system “milk” and the sour milk products obtained based on it;

– to optimize technological processes associated with the stabilization of the systems “milk” and “dairy products” through control over kinetic equilibrium, which is estimated based on the magnitudes of coefficients k_1, k_2, k_3, k_4;

– to intensify the processes for obtaining sour-milk products through instantaneous impacts on the technological vectors of processes by shifting the ratio of weight coefficients (pairwise) k_1, k_2 and k_3, k_4;

– to develop fundamentally new, in terms of approaches and intensity, technologies for processing the system “milk”, which, according to the law of mass preservation, determine the magnitude and stability of coefficients $k_1 ... k_4$.

6. 1. Testing of the model in the framework of technological process of production of milk fat with adjustable thermal stability

An analysis of equation (6) allows us to describe the state of any milk product or a sour milk product, including fresh milk. Thus, the composition of drinking milk includes several forms of calcium:

– micellar, which is in the composition of casein-calcium-phosphate complex, as well as phosphate and citric salts in the form of a colloidal phase;

– ionic, which is in the form of free Ca^{2+} ions.

The research results revealed that during milk storage its composition undergoes internal redistribution between forms of calcium at simultaneous stable indicator of its overall content. In this case, a decrease in the active acidity of milk (that occurs even during a short storage) leads to the accumulation of ionic calcium. This is accompanied by the emergence of undesired potential, which is caused by a decrease in the colloidal resistance of milk to technological factors, in particular thermal effect.

However, the stability of milk as a technological system during storage and under the influence of technological factors is associated with a growth in coefficient k_2, which is the result of decomposition of casein micelles and the release of Ca^{2+}. This is contributed to by a change in the biochemical and microbiological potential of the system that affects the accumulation of lactic acid. Establishment of new conditions for equilibrium is due to a decrease in pH, that is, accumulation of Ca^{2+} in the system. Since the main condition for the integrity of the system is its colloidal stability, then it is obvious that the main destabilizing factor of equilibrium is the concentration of ionized calcium in the system.

With respect to such a formal interpretation of transitions, the system of technological activities becomes clear; it involves a reduction in the capacity of the system, that is, the neutralization of the active (ionic) form of calcium.

By realizing that milk is a unique product, changing whose composition is undesirable and, in many cases, prohibited, it is appropriate to influence a change in the potentials of the system “milk” by applying principles of intraphase interaction. The principle of the intraphase interaction implies that the substance-corrector never forms real or colloidal solutions in the system “milk” or in the products of its processing. This substance is always in the state of a separate phase, relative to the solvent in the system “milk”, which can be completely removed from milk by means of specialized technological techniques. However, being at the same time in milk in the state of a phase with a certain level of intactness, they have between them a certain material and energy exchange, which is the reason for bringing down the undesirable potentials of milk.

The consequence is the shape-formation with the emergence of a new phase, which may be associated with both the ability of calcium ions to create salt bridges and, under certain conditions, to form coordination relations.

Such substances include a natural sorbent of calcium ions – sodium alginate, adding which to milk leads to the ion exchange through the surface of phases, resulting in the enhanced phase intactness. This principle is very effective and efficient because milk always contains ion calcium whose diffusion into a sodium alginate solution ensures the formation of a solid phase of calcium alginate. In this case, intactness of the solid-phase increases with the growing degree of substitution with guloron and mannoron blocks of uronic residues of sodium alginate. This significantly reduces the chemical potential of milk, a positive gain in the magnitude of entropy increases, which leads to the stabilization of a dairy product.

The process of binding calcium ions in milk and the removal from the system were carried out in the following way. We added to skimmed milk at a temperature of 4–6 °C a solution of sodium alginate under a drop mode, and then maintained for (55–60)·60 s. The result of the ion-exchange reaction between calcium ions of milk and sodium alginate in the system “milk” is the formation of a new phase – calcium alginate. This phase was isolated from milk by decantation (Fig. 3).

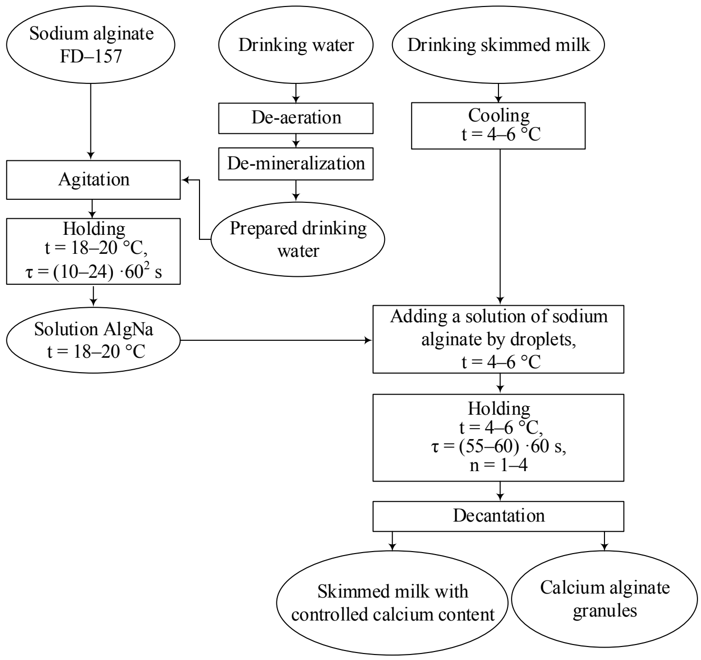

Fig. 3. Model of technological process for producing skimmed milk with controlled calcium content by the amount and forms

Such a process of milk decalcification makes it possible to isolate up to 40 % of calcium from the system of all its starting content, under condition that the specified process occurs in n stages. The number of stages will always depend on the starting content of calcium in the system "milk". It should be noted that the proposed method for milk decalcification will occur owing to the redistribution of calcium between the free and the colloidal forms. This does not reduce the nutritional value of the system "milk" through the removal of organic calcium from the composition of casein micelles.

The kinetics of sorption of Ca^{2+} ions by a sodium alginate solution and the redistribution of relative content of micellar and ionic calcium in the system "milk" are shown in Fig. 4.

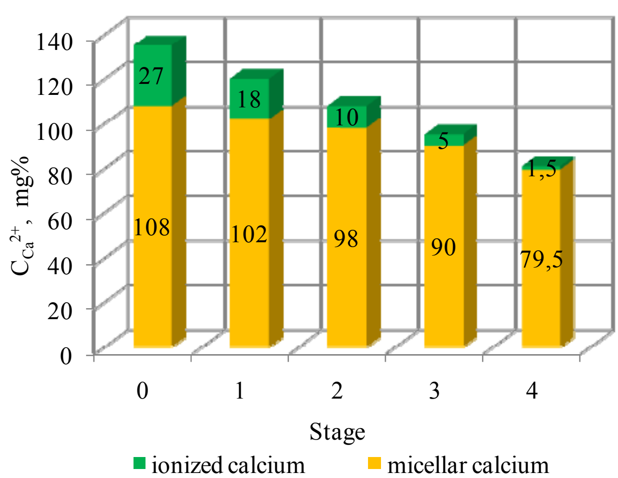

Fig. 4. Kinetics of sorption of Ca^{2+} from skimmed milk by a solution of sodium alginate

It was established that the process of milk decalcification is advisable to perform in several stages (n=1–4) depending on the starting content of calcium in the system "milk". In this case, the use of AlgNa (in the form of aqueous solutions) through the course of a substitution reaction translates Ca^{2+} into insoluble state, thus disrupting the equilibrium of $k_1=k_2$ towards $k_2>k_1$. Note that at each stage of the removal of ionic calcium from the system "milk" there occurs the internal redistribution of calcium in the system. This manifests itself in a decrease in the share of micellar form with the simultaneous accumulation of calcium in the ionized state, as well as a change in the properties of the system in general. However, a decrease in calcium in the system "milk" to 80 mg % does not lead to the internal redistribution, while the intensity of the accumulation of ionized calcium is minimized. It follows that milk decalcification to the level of 80–90 mg % creates conditions under which equation is implemented in full (7).

Based on the specified conditions of stability in the systems "milk" (7), it becomes possible to predict a change in the functional and technological properties of the latter, specifically, an increase in the resistance to the influence of technological factors.

With respect to the undertaken research regarding the phased introduction of sodium alginate, we considered it appropriate to investigate the thermal stability of skimmed milk using an alcohol test depending on the amount of Ca^{2+} sorbed and removed from the system (Table 1).

Table 1

Dependence of thermal stability of the system "milk" on the amount of sorbed Ca^{2+}

Alcohol concentration, %	Thermal stability of the system "milk" depending on the amount of sorbed Ca^{2+}				
	0	10	20	30	40
60	–	+	+	+	+
65	–	–	+	+	+
70	–	–	–	+	+
75	–	–	–	–	+

An analysis of data in Table 1 and Fig. 2 allows us to assert that the process of regulation of calcium content in the system "milk" leads to an increase in its thermal stability. This is explained by the fact that the removal of up to 40 % of calcium from the system "milk" leads to the decomposition of casein micelles into smaller submicelles. This is accompanied by an increase in the overall charge of a protein molecule and an increase in its hydrate layer. The latter manifests itself by the effects in the colloidal stability of the systems relative to a thermal influence. In other words, the system "milk" reaches the state, which is maximally close to the state of absolute thermodynamic equilibrium, which is described by equations (7)–(9).

The regularities established are in full agreement with those studies by scientists [34–36] that indicate the relationship between the content of ionized calcium and milk thermal stability.

Thus, the implementation of conditions for the stability of milk according to equations (7) can be achieved by the decalcification of milk to certain limits. In this case, the process of decalcification to the level of 40 % enables the fulfillment of conditions for equilibrium (8) and (9).

It should be noted that the introduction of the proposed method for stabilizing milk might form the basis for the development of a wide range of technologies of combined products based on the dairy and fruit-berry raw materials that are, at reduced pH values, characterized by colloidal stability under thermal effect [37].

6. 2. Verification of the model in the framework of implementation of the technological process for manufacturing sour milk cheese

Underlying the technological process for manufacturing sour milk cheese are the principles of colloidal destabilization of milk casein and its isolation into a separate phase followed by the removal from the system. Milk protein coagulation is not a self-induced and isolated process. This process occurs against the background of other processes, such as the hydrolysis of milk carbohydrates, lowering pH and, as a result, a change in the salt equilibrium with the accumulation of ionic calcium. In essence, coagulation is a visible result of the complex influence on milk proteins, specifically casein, and reducing its colloidal stability.

Data in Fig. 3 show that the process of fermentation and the formation of protein clot are accompanied by lowering pH of the system with the simultaneous accumulation of ionic calcium. The duration of this process is traditionally determined by pH, which at the end of the process must reach values of 4.5–4.7, and is typically $(6-10)\cdot 60^2$ s. Note that an increase in the active acidity of protein clot occurs fairly uniformly, from 6.8 to 4.7, over a time interval of $(0-4)\cdot 60^2$ s. Further fermentation leads to the slowing down in the accumulation of hydrogen ions. Over a time interval of $(6-8)\cdot 60^2$ s active acidity reaches 4.5–4.6 and remains almost unchanged over the last two hours in the technological process.

At the same time, the same patterns are observed during accumulation of ionic calcium in the system. As data in Fig. 5 indicate, a maximum in the concentration of calcium ions is observed at hour 6 of fermentation, which corresponds to active acidity on the level of 4.5.

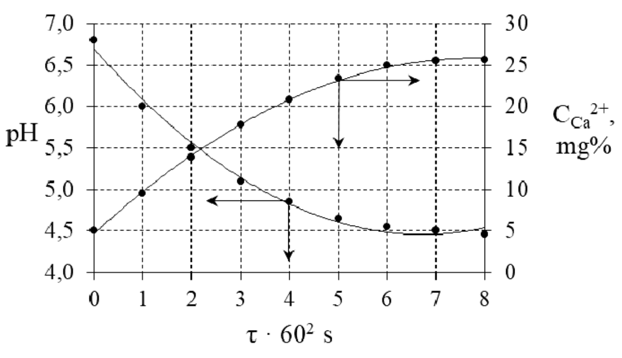

Fig. 5. Dynamics of active acidity and accumulation of ionic calcium in the fermentation process of the system "milk"

Thus, one can see that the process of fermentation leads to the redistribution of micellar and ionic forms of calcium in the system. This offsets equilibrium in the system in the direction of the accumulation of ionic calcium, at which patterns of expressions (10)–(15) are clearly implemented.

It becomes obvious that the main factors that affect the rate of coagulation process are the intensity of lowering pH of the system with the simultaneous accumulation of ionized calcium. In order to intensify the process of fermentation, it is proposed to create systems based on milk that meets criteria (7), and serum with characteristics that match (12), (13). Characteristic of the model systems based on milk and serum is given in Table 2.

Table 2

Characteristic of the model systems based on milk and serum

Ratio milk:serum	pH of the system	C_{Ca}^{2+}, mg%	Fermentation period ·60, s	The yield of sour milk cheese, % (calculated to the mass fraction of milk in the system)
100:0	6.70	6.2±0.1	480	15.2±0.5
90:10	6.25	7.9±0.1	390	15.7±0.5
80:20	5.80	11.0±0.1	300	15.2±0.5
70:30	5.50	14.1±0.1	150	15.3±0.5
60:40	5.39	16.4±0.1	75	15.8±0.5
50:50	5.28	19.1±0.1	30	15.4±0.5

Data in Table 2 show that an increase in the content of serum in the system from 0 % to 50 % leads to a logical decrease in pH of the system from 6.7 to 5.28. At the same time, we observed an increase in the content of ionic calcium by 3.1 times – from 6.2 to 19.1 mg %.

An increase in active acidity of the system leads to breaking the structure of casein-calcium-phosphate complex with such a structural element as calcium phosphate being cleaved. In addition, under the influence of lactic acid there occurs the transformation of phosphates and citrates, contained in serum, into soluble forms of calcium lactates:

$$CaHPO_4 + 2C_3H_6O_3 \rightarrow (C_3H_5O_3)_2Ca + H_3PO_4, \quad (18)$$

$$Ca_3(C_6H_5O_7)_2 + 6C_3H_6O_3 \rightarrow 3(C_3H_5O_3)_2Ca + 2C_6H_8O_7, \quad (19)$$

which are capable under certain conditions of dissociating with the accumulation of free ionized calcium in the system.

In the course of fermentation of the examined samples, we controlled the dynamics in a change in active acidity and the accumulation of ionic calcium (Fig. 6, 7).

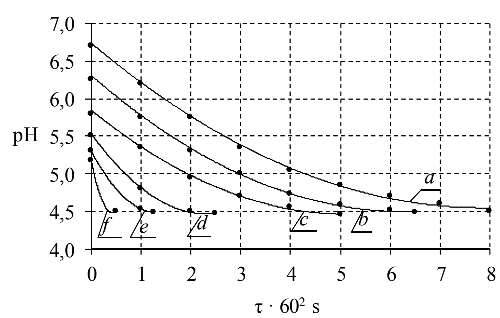

Fig. 6. Dynamics of active acidity in the system "milk" during fermentation at the ratio milk:serum: *a* – 100:0; *b* – 90:10; *c* – 80:20; *d* – 70:30; *e* – 60:40; *f* – 50:50

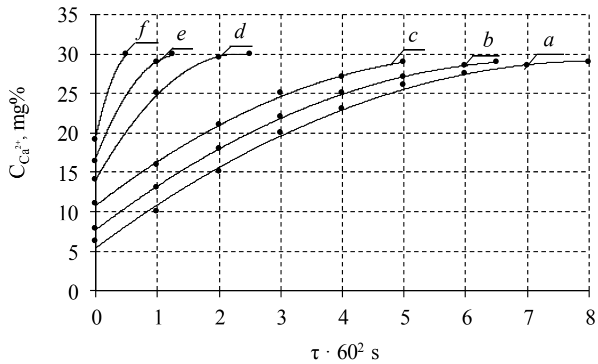

Fig. 7. Dynamics of the accumulation of ionic calcium in the system "milk" during fermentation at the ratio milk:serum: *a* – 100:0; *b* – 90:10; *c* – 80:20; *d* – 70:30; *e* – 60:40; *f* – 50:50

An analysis of Fig. 6, 7 (curves *a*–*c*) reveals that in the interval of fortification of the systems from 00:0 to 80:20 the dynamics of decrease in pH and the accumulation of ionic calcium in the system is expressed by an almost linear dependence that plateaus at reaching a pH of 4.5 (the amount of ionized calcium is 27.0±0.1 mg %). An increase in the degree of thinning the systems from 70:30 to 50:50 changes the character of the curves (Fig. 6, 7, curves *d*–*f*). In this case, kinetics of the process increases significantly while length of the process is decreased by about 3.5–16 times.

It should also be noted that a further increase in the degree of thinning is not appropriate since increasing the mass fraction of serum in the system above 50 % leads to a sharp reduction in pH to 4.7–4.9. This in turn destabilizes the system "milk", which is accompanied by its stratification into a serum fraction and a solid protein phase in the form of flocculates.

Based on the results of studies conducted, we developed a model of the technological scheme for producing cottage cheese, which implies intensification of the technological process of its manufacture by reducing the time of fermentation and obtaining a protein clot to 30 minutes (Fig. 8). A special feature when conducting a given process is a preliminary preparation of mixture for the fermentation. The essence of the process is in a controlled blending of milk and serum to the fixed values of pH at the level of 5.28, which corresponds to the total content of ionized calcium at 19.1±0.1 mg %.

Note that in a given example we considered a case of using fresh milk (pH=6.7–6.8). However, in this technological process there is the possibility to apply a different degree of dilution, which will be predetermined by the concentration of calcium ions and pH of milk as a raw material. The main parameters, which would require control in this case, are the objective characteristics of the mixture for fermentation (the value of pH and the content of ionized calcium).

Next, we add to the prepared mixture a fermentation culture for direct introduction. It should be noted that in the intensified technology the role of leaven mainly implies the formation of organoleptic properties of products, that is, the formation of aromatic substances that will define the characteristic taste and aroma of the finished products. At the same time, the role of the leavening culture in reducing pH of the system will be kept to a minimum. Accordingly, the amount of leavening culture, which is necessary for the formation of organoleptic properties of cottage cheese, can be adjusted and reduced by 2–3 times in comparison with the classic technology. The process is subsequently performed in line with a classic technology that includes the process of system fermentation, cutting and heating the clot, self -pressing and cooling. In this case, conducting the technological process with the preliminary controlled blending of the systems leads to the intensification of fermentation process. Duration of the process decreases by 16 times – from 480·60 s to 30·60 s.

The serum, received during self-pressing of the clot, under certain technological influences (if necessary) can act as a system whose state meets criteria (13). That is, it can shift the state of equilibrium in the system "milk" and thereby opens up new prospects for its processing. The resulting system becomes cyclically closed making it possible to implement the principle of comprehensive processing of milk raw materials.

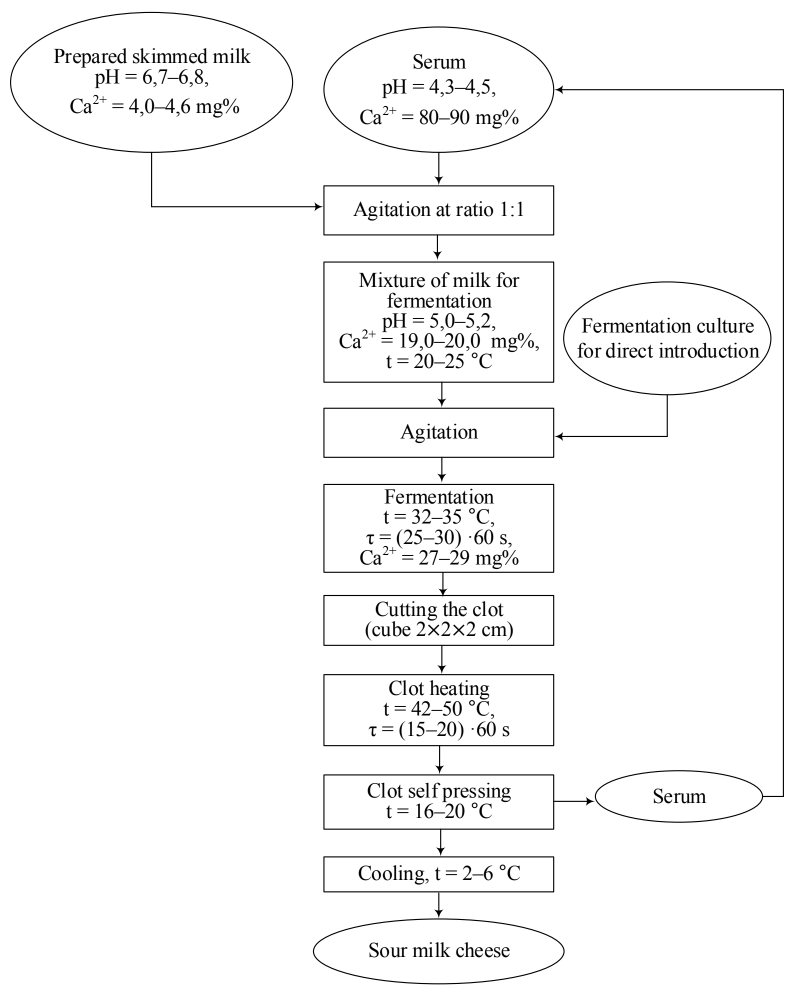

Fig. 8. Model of the technological scheme for producing sour milk cheese using the intensified technology

Based on data in Table 2, it should be noted that the yield of cottage cheese at the intensification of technological process when estimated for the content in the system of milk is a constant magnitude and does not practically depend on the degree of dilution with serum.

We conducted a comparative analysis of organoleptic indicators of cottage cheese obtained using classic and the intensified technology. It was established that in terms of organoleptic indicators the sour milk cheese manufactured according to the intensified technology does not differ from control. Moreover, in terms of "consistency" and "taste", it exceeds them. This is due to the fact that the process of fermentation in the system "milk" with obtaining a protein clot occurs fast enough under controlled parameters that prevent overfermentation of the system. Thus, the taste of the product becomes clearly expressed sour-milk, not sharp, no foreign aftertaste. Similar patterns are observed when analyzing consistency. Control over ionic calcium content in the system during fermentation leads to obtaining cottage cheese with a layered, plastic texture, with pronounced grain, without serum.

Thus, the sour milk cheese whose state can be described by equation (17) can be obtained by blending the system "milk" with characteristic attributes according to (6) with the transformed system that meets the criteria of equation (13). It is possible to use as such a system milk serum in ratios that enable reaching the state of the system described by expression (17).

It is promising from a scientific and practical point of view to apply the developed model for a variety of dairy and sour-milk products. It becomes clear that, first, there is a need to describe a particular dairy product according to equation (17). And the next stage implies, by controlling the calcium content (adding it or removing it), obtaining such technological systems that at minimal technological influence can be transformed into specific milk or a sour-milk product.

7. Conclusions

1. We established a dependence between the amount and state of calcium in milk and its technological purpose. It is shown that the derived dependence, in combination with technological objectives, can be accepted at the first stage as the basis for predicting (estimation) quality level of a sour milk product, and at the second stage – for determining the conditions and parameters of its stabilization in the technological process.

2. It was proven in the course of mathematical modeling that a controlled change in the ratio of enthalpy and entropy factors makes it possible to create new principles for the stabilization of the system "milk", while identifying regularities in the emergence of new potentials determines the possibility of using it in the fundamentally new technologies, based on the implementation of these potentials, which leads to the intensification of technological processes.

3. We verified the adequacy of theoretical model of the colloidal stabilization of the system "milk" by controlled regulation of the amount and forms of calcium in the system. It was established that stability of the colloidal phase of milk depends on the existence of potential in the system in the form of accumulation of free calcium ions. Reducing the level of the latter through decalcification with a controlled formation of the new phase leads to an increase in the colloidal stability of the system "milk" under the influence of technological factors.

4. We verified the adequacy of theoretical model of the intensification of technological process for producing cottage cheese. It was proven that the controlled adjustment of ionized calcium and pH of the system makes it possible to intensify the technological process of manufacturing sour milk cheese. Such effect is achieved by blending the system "milk" with the transformed system (serum) in certain amounts, which ensures obtaining products with improved organoleptic properties.

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