UDC 637.134
DOI: 10.15587/1729-4061.2018.133365

ANALYSIS OF BACKGROUND AND DEVELOPMENT OF TECHNOLOGICAL PRINCIPLES OF MILK PROCESSING BY COUPSULATION

N. Grynchenko
PhD, Associate Professor*
E-mail: tatagrin1201@gmail.com
P. Pyvovarov
Doctor of Technical Sciences, Professor**
E-mail: pcub@ukr.net
O. Nagornyi
PhD, Associate Professor**
E-mail: niv1112@ukr.net
*Department of Meat Processing Technologies***
Department of Food Technologies*
***Kharkiv State University of Food Technology and Trade
Klochkivska str., 333, Kharkiv, Ukraine, 61051

Доведено, що молоко як сировина володіє унікальним потенціалом. Визначено, що найбільш ефективним шляхом використання потенціалу молочної сировини, зокрема потенціалу іонів кальцію, є застосування технічного рішення одержання капсульованих форм молочної сировини на основі альгінату натрію. Даний процес реалізовано через принцип крапельної екструзії молочної сировини через повітря в розчин високомолекулярної сполуки-поліелектроліту – альгінату натрію. Підтверджено, що потенціал системи «молоко» за кальцієм є малодинамічним та неефективним. Встановлено, що здійснення активації визначених потенціалів можливо як за рахунок зниження pH системи «молоко» впродовж сквашування, так і за рахунок її купажування з системою «сироватка». Виявлено, що купажування молока і сироватки з виникненням нової системи «молоко-сироватка» з необхідним рівнем концентрації іонів кальцію не впливає на колоїдну стабільність молока. З іншого боку – надає системі «молоко» високоефективного низькоенергетичного потенціалу у вигляді потенціалу іонів кальцію, що дозволить ефективно реалізовувати процес її капсулювання. Обґрунтовано, що відкрита технологічна система «молоко» може бути переведена у систему з обмеженою відкритістю «молоко-сироватка» у капсульованій формі, а значить і з мінімізованим впливом збурюючих факторів, тобто з підвищеною керованістю технологічних процесів. Експериментально підтверджено, що купажування систем «молоко» та «сироватка» у співвідношення 70:30 є необхідною умовою накопичення критичної концентрації іонного кальцію (24–25 мг %). Це забезпечує одержання капсульованої продукції правильної кулеподібної форми. Одночасно таке співвідношення компонентів не на значно змінює pH суміші, що також є важливим критерієм реалізації процесу капсулювання. Розроблено модель технологічного процесу переробки молока шляхом капсулювання. Доведено, що розроблений підхід повною мірою дозволяє реалізувати потенціал молока з одержанням харчових продуктів з новими споживчими властивостями.

Ключові слова: молочна сировина, переробка молока, термодинамічний потенціал, іонний кальцій, альгінат натрію, капсулювання, інкапсулянт

1. Introduction

One of the components of sustainable development of the state is ensuring its economic and food security which is determined by the provision of food resources, economic availability, quality assurance. Solution to this problem also lies in the plane of elaboration and realization of resource-saving technologies aimed at import substitution, rational use of raw materials and development of products with new consumer properties.

In today's conditions, one of the ways to meet the consumer demand for high-quality and wholesome food products consists in combining conventional technological approaches with the latest scientific and technical achievements. That is why scientific and practical lines in processing milk to ready-for-use and semi-finished products should be based on fundamental and applied studies in the dairy industry.

For today, bearing in mind the intensive development and introduction of innovative technological solutions in the dairy industry, processing of milk as a raw material is mostly based on classical technologies. Most of them are aimed at ensuring conditions for milk stability or are based on the principles of maximum use of its nutrients.

This does not allow producers to fully realize potentials of milk as a technological system for obtaining food products with new consumer properties.

All of this determines necessity of development of modern technologies for processing milk and dairy products to create products fundamentally new in their structure, merchandising characteristics, and organoleptic indicators.

One of such approaches is based on the change of chemical potential of milk salts with accumulation of calcium ions in whey in the process of preparing sour-milk products. In many classical technologies, growth of the chemical potential of calcium ions is a side effect of the technological process. At certain concentrations, it may negatively affect quality of end products.

At the same time, scientifically and technologically grounded use of the potential of calcium ions of milk and milk products will enable introduction of new technological principles in the milk processing technology. The base effects here are the effects of resource conservation, higher efficiency, and creation of high added value. Therefore, scientific substantiation and development of the technology of encapsulated dairy products based on utilization of the chemical potential of ionic lactocalcium is timely and in demand.

Urgency of the study consists in the necessity of scientific support for realization of fundamentally new technologies based on the use of secondary raw materials (for example, whey) in the workflow of milk processing. Whey obtained in production of sour milk cheese is essentially an effective source of ionic calcium. It can significantly affect the dynamic potential of milk processed on the basis of the proposed technological principles.

These principles are based on interaction of ionic calcium of milk and whey with ionotropic polysaccharides. The result is a controlled forming of the technological systems for production of new food products in a form of capsules (spheres with gel-like shells and liquid dairy products inside) or granules (spheres with a solid gel-like structure). By their classification specifiers, products with this structure belong to structured food products forming the market sector that is developing rapidly in the global food business.

For milk and dairy products, these approaches are fundamentally new and when scientifically justified, may become a basis for creating new scientific and technological trends.

2. Literature review and problem statement

The innovations based on a creation and use of new technologies form a vector of qualitative improvement of dairy products. It should be noted that innovative products provide a stable growth of the entire product range amid stagnation of the conventional assortment. The new technologies are precisely those that purposefully form a complex of physical-chemical and organoleptic indicators of products through the use of new technological solutions, in particular, involvement of new ingredients [1].

Over the recent years, a steady tendency towards a significant growth in the sectors producing milk for drinking, sour milk products, cheese, yogurt, and milk desserts was observed. Traditionally, the largest shares in the volume of dairy products au naturel belong to milk for drinking: 57 %, sour milk products: 24.9 %, rennet cheese: 6.7 %, butter: 5.9 %, dried dairy products: 3.4 %, sour milk cheese: 4.1 % and casein and caseinates: 0.3 % [2].

However, for today, milk processing is based on classical approaches and the innovation proposals concern ingredient composition and hardware support [3, 4].

Present-day technological aspects of milk processing are also connected with the use of ion-exchange processes and membrane technologies, creation of functional dairy products.

The use of ion-exchange processes in the dairy industry makes it possible to influence composition of the initial raw material and the product as well as find new ways to intensify the processes of production, preservation and improvement of milk taste [5]. In this case, the use of sorbents makes it possible to change salt composition of milk, reduce its acidity and increase thermal stability, desalinate whey, and remove lactic acid from it [6].

Membrane technologies (ultrafiltration) are also actively used in milk processing. Due to their multidimensional nature, they can be used in a large number of separation processes. Ultrafiltration is a baromembrane process of separation in which membranes do not pass particles and macromolecules the size larger than 2...3 nm. The membrane technology is based on the properties of dairy raw materials with a pronounced selectivity of components in molecular weight, particle size and ionic strength. The main objective of ultrafiltration is production of protein concentrates with various contents of dry matter [7, 8].

One of the lines in production of functional dairy products is development of products for certain consumers. This group includes products for infant nutrition, gerontological dietetics [9], fitness nutrition and dietary purposes [10]. In this case, formulation composition and the process of production of such products should meet the needs of a certain group of consumers for certain macro- and micronutrients. It is achieved by increasing (protein) or reducing (lactose) the content of certain components of dairy raw materials as well as enrichment of products with essential nutrients [11].

The technologies for production of functional dairy products and products with probiotic properties are of particular relevance. Among the wide variety of probiotic microorganisms, bifidobacteria are the most common since they are the basis of a normal human intestinal microflora [12]. It is known that dairy products with probiotic properties contribute to higher digestibility of calcium and increase secretion of gastric juice. They inhibit development of undesirable microflora due to their bactericidal action [13], contribute to lowering of cholesterol level, have a stimulating effect on the immune system [14].

Such a typical approach does not allow one to consider milk as a raw material possessing significant thermodynamic and chemical potentials. This becomes the basis for forming a new view on the functional and technological properties of dairy raw materials as a system because there is an opportunity to form new approaches to processing based on identification of these potentials. At the same time, no study has been found in which milk or products of its processing can be used as a liquid technological medium (encapsulant) with certain properties and characteristics. This will enable performance of new technological operations involving third substances that respond to identified chemical and/or technological potentials. In this case, an opportunity arises to transform the high enthalpic factor into entropic one, thereby stabilizing the system with formation of new physical forms (capsules).

Introduction of this technology into production will ensure a more efficient use of the nutritional potential of dairy raw materials by using whey and creating new structured products. In this case, creation of a gel-like capsule shell will ensure transition of the “open” technological system to a partly “closed” one which is the latest principle of processing milk and dairy products.

3. The aim and objectives of the study

This work objective was to develop technological principles of milk processing by encapsulation and determine conditions for their realization. This approach involves a secondary dairy raw material (whey) in the process of production which is the determining factor in the control of milk potentials in terms of accumulation of ion calcium and realization of the encapsulation process.

To achieve this objective, the following tasks were solved:

– to formulate a working hypothesis which in a case of its confirmation will make it possible to develop technological principles of effective processing of dairy raw materials into the dairy products which are fundamentally new in their composition and form;

– to study milk and dairy products (whey) as a system for assessing the possibility of using the chemical potential of calcium ions in the technology of encapsulated milk products;

– to analyze the conditions for realization of the process of encapsulation of “milk”, “whey”, “milk-whey” systems for realization of the potential of calcium ions;

– to determine rational parameters of blending “milk” and “whey” systems with ensuring of technological characteristics of the blend for realization of the encapsulation process.

4. The materials and methods used in the study of “milk”, “whey”, “milk-whey” systems

The study subjects used:

– skim milk delivered by Zmiyivsky Dairy Plant CJSC (Zmiyiv, Ukraine);

– whey produced by Zmiyiv Dairy Plant CJSC (Zmiyiv, Ukraine);

– milk and whey blends;

– complex forming agent: FD-157 sodium alginate (AlgNa) manufactured by Danisco Co., Denmark) and authorized by the Central executive body in the field of health care, Ukraine, for the use;

– encapsulated milk.

Milk and whey blends were obtained by blending milk raw materials in a milk:whey ratio of (100:0)–(0:100).

Encapsulated products were obtained under the production conditions of Kapsular LLC by means of an encapsulation device whose operation principle is given in [15].

The following methods and procedures were used in the study.

To describe thermodynamic systems, so-called state parameters and state functions were used which only made sense for an integral system taking into account properties of its individual components [16]. For thermodynamic description of nonequilibrium processes, the concept of thermodynamic potentials was used.

The mass fraction of ionized calcium in the test samples was determined by a potentiometric method using a calcium-selective electrode [17]. The active acidity of skimmed milk was determined using a pH meter of pH-150 MI (Measuring Technologies Co., Russia) with an electrode system for measuring pH. To estimate globularity of the capsules, their form factor was determined based on the ratio of their maximum diameter (d_{vertical}) to the minimum diameter ($d_{\text{horizontal}}$).

$$K_f = \frac{d_{vertical}}{d_{horisontal}} \approx 1. \tag{1}$$

Provided $K_f \approx 1$, capsules have a spherical form, if $K_f < 1$, capsules are close to the oval shape. Capsules were considered spherical if their form factor was 0.9...1.0.

Experimental studies were carried out in the Laboratory of Rheological Studies at Kharkiv National Food and Trade University (Ukraine).

5. Analytical and experimental studies of behavior of ionic calcium accumulation in dairy products

A working hypothesis was formulated as follows: determination of values of thermodynamic potentials of milk in a workflow makes it possible to choose an effective way of its processing and ensures intensification of technological processes.

According to the innovation idea, it was envisaged to use the potential of free calcium ions in the technology of obtaining “whey” and “milk-whey” systems encapsulated in an alginate-calcium shell for realization of the chemical potential of calcium ions in dairy raw materials: lactocalcium:

$$\begin{aligned} & n(\mathrm{Alg}^{-}\cdot Na^{+}) + m(Ca_{Lac}^{2+}) \rightarrow \\ & \rightarrow \left[nm(A\lg_2 Ca_{Lac} \downarrow)\cdot n - nm(A\lg^{-}\cdot Na^{+})\cdot m - \right. \\ & \left. - mn(Ca_{Lac}^{2+}) \right] + 2nm(Na^{+}), \end{aligned} \tag{2}$$

where

$$\left[nm(A\lg_2 Ca_{Lac} \downarrow)\cdot n - nm(A\lg^{-}\cdot Na^{+})\cdot m - mn(Ca_{Lac}^{2+}) \right]$$

is the composition of gel alginate-calcium shells at the existing concentrations [AlgNa] and ionic lactocalcium [Ca_{Lac}^{2+}].

Analytical and experimental information on the objectivity and behavior of accumulation of calcium ions when changing pH of milk into acidic zone is important for controlling of this process. Behavior of accumulation of calcium ions in milk was determined for pH variation in the ranges characteristic for making sour milk products (Fig. 1, 2).

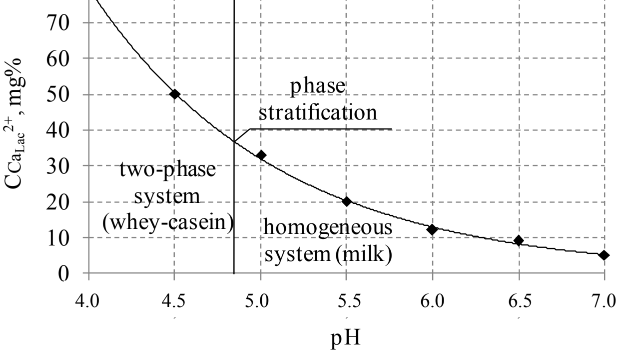

Fig. 1. Dependence of accumulation of calcium ions in “milk” and “whey-casein” systems on pH (t=20±0.1 °C)

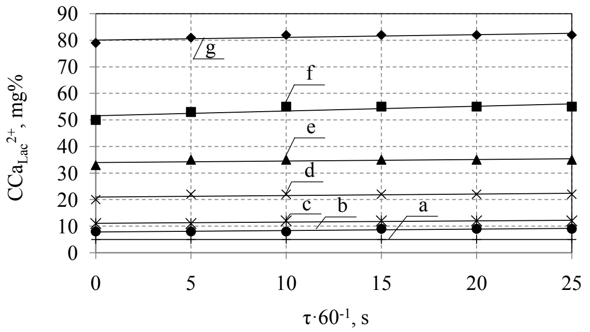

Fig. 2. Dynamics of pH-static concentration of calcium ions in milk and dairy products (t=20 °C) at pH: 7.0 (a); 6.5 (b); 6.0 (c); 5.5 (d); 5.0 (e); 4.5 (f); 4.0 (g)

It should be noted that the process of release of ionic calcium in time objectively depends on the system pH (Fig. 1) and its concentration practically does not change in pH-static conditions (Fig. 2). For example, the minimum content of calcium ions at a level of about 5 mg % was observed at pH 7.0. A corresponding decrease in pH to 4.0–5.0 leads to a 7 to 16-fold increase in concentration of ionized calcium which reaches the maximum value of 80.0 mg % at pH 4.0.

It is technologically important that keeping milk products (milk, whey) at fixed pH values practically does not affect change in the content of ionic calcium in the system (Fig. 2).

When extruding milk into a solution of sodium alginate and proceeding from the actual composition of mineral substances by solubility, it can be predicted that the share of $nm(A\lg_2 Ca_{Lac}\downarrow)$ in the “milk” system (pH 7.0) will be negligible. This relates to the fact that the concentration $C_{\mathrm{Ca}_{Lac}^{2+}}$ as the only participant capable to block sodium alginate in milk is insufficient (roughly 4.0–10.0 mg %).

It means that at neutral values of milk pH, it is obvious that a generalized record of gel formation (formation of a separated gel-like phase) for the “milk” system can be represented in a general form as:

$$(A^-\cdot b^+)_n + B^+ \xrightarrow{k_1}\xleftarrow[k_2]{} (\mathrm{A}^-\cdot b^+)_n - \\ -(A^-\cdot B^+)_{n-x} + (n-x)\cdot b^+, \tag{3}$$

where B^+ is the ionic calcium available in milk at a determined anti-ion; $(\mathrm{A}^-\cdot b^+)_n - (A^-\cdot B^+)_{n-x}$ is the excess sodium alginate in the system.

When evaluating equation (3), it is evident that milk encapsulation is technologically impossible under such conditions. This is because there is no free ionic calcium in the right side of expression (3). According to Fick’s law, it is not capable of diffusion into the sodium alginate phase with its chemical potential ensuring formation of the capsule walls. Gel formation in general and encapsulation as an innovative technological idea is only possible if gel is formed at an excess amount of ionic calcium. This is realized at the expense of appearance of the state $nm(A\lg_2 Ca_{Lac}\downarrow)$ (2) with the formation of a physical interface of a spherical form.

It is possible to evaluate such an effect for calcium alginate gels based on the product of three indicators, namely:

– C_{AlgNa}: the molecular concentration of sodium alginate;

– C_{GA}: the content (mass concentration) of guluronic acid in this type of sodium alginate. This indicator makes it possible to consciously make selection of a functional substance since $\frac{C_{\mathrm{GA}}}{C_{\mathrm{MA}}}$, i. e. the ratio of mass particles of α-L-guluronic and β-D-mannuronic acids in the composition of alginic acid determine its ability to gel formation. If $[C_{\mathrm{MA}}]>>[C_{\mathrm{GA}}]$, there will be no gelation;

– $\chi=\frac{C_{\mathrm{GA}}^{2+}}{C_{\mathrm{GA}}}$: has the sense of degree of realization of reaction of a cooperative type the level of which is used in assessment of quantitative values of reaction completeness.

Provided that

$$\chi=0, \tag{4}$$

the system is characterized as a solution of sodium alginate;

$$\chi=0{,}1-0{,}3, \tag{5}$$

the system is characterized as a thickened system;

$$\chi=0{,}4-0{,}6, \tag{6}$$

the system is characterized as gel (calcium alginate) which provides complexation with composition of the $(A\lg_2 Ca_{Lac}\downarrow)$ system in a prevailing mass concentration.

Taking into consideration the kinetics of the process and the order of the chemical reaction for the spherical structure of the drop, the kinetic process of capsule formation can be objectively expressed from the law of active masses:

$$-\frac{d[A\lg Na]}{d\tau}=\frac{d[A\lg_2 Ca_{Lac}]}{d\tau}=k\left[A\lg^-\right]\cdot\left[Ca_{Lac}^{2+}\right]. \tag{7}$$

At an unknown concentration of calcium, taking into account the above, the expression takes the form:

$$-\frac{d[A\lg Na]}{d\tau}=\frac{d[A\lg_2 Ca_{Lac}]}{d\tau}= \\ =k\left[A\lg^-\right]\cdot\left[C_{A\lg^-}\cdot C_{GA}\cdot\frac{C_{GA}}{C_{MA}}\cdot\chi\right], \tag{8}$$

where

$$\left[\mathrm{Ca}_{Lac}^{2+}\right]=\left[\mathrm{C}_{A\lg^-}\cdot C_{\mathrm{GA}}\cdot\frac{\mathrm{C}_{\mathrm{GA}}}{\mathrm{C}_{\mathrm{MA}}}\cdot\chi\right]. \tag{9}$$

Expressions (8) and (9) determine minimum concentration of calcium ions to ensure the encapsulation process. In this case, concentration of guluronic acid (C_{GA}) and its ratio to the mannuronic acid (C_{MA}) in the composition of alginic acid $\frac{C_{\mathrm{GA}}}{C_{\mathrm{MA}}}$, as well as the degree of substitution χ. are important.

The practical meaning of the expression $\chi=\frac{C_{\mathrm{GA}}^{2+}}{C_{\mathrm{GA}}}$ is actually reduced to occurrence of case (6), that is, the magnitude of 0.4–0.6. Bearing in the mind that the remainders of guluronic acid are only a part of the structure of sodium alginate but fully (100 %) responsible for gelling, that is, in fact there is a situation where:

$$\chi=\frac{C_{\mathrm{GA}}^{2+}}{C_{\mathrm{GA}}}=\left[A\lg_2 \mathrm{Ca}_{Lac}\right]. \tag{10}$$

Taking into account the above, the expression can be written as:

$$-\frac{d[A\lg\mathrm{Na}]}{d\tau}=k\left[A\lg^{-}\right]\cdot\mathrm{C}_{\mathrm{Alg}^{-}}\cdot C_{\mathrm{GA}}\cdot\frac{\mathrm{C}_{\mathrm{GA}}}{\mathrm{C}_{\mathrm{MA}}}\cdot\left[A\lg_2\mathrm{Ca}_{Lac}\right]. \quad (11)$$

whence:

$$\left[A\lg_2\mathrm{Ca}_{Lac}\right]=\frac{k\left[A\lg^{-}\right]\cdot\left[C_{\mathrm{Alg}^{-}}\cdot C_{\mathrm{GA}}\cdot\frac{C_{\mathrm{GA}}}{\mathrm{C}_{\mathrm{MA}}}\right]}{-\frac{d[A\lg\mathrm{Na}]}{d\tau}}. \quad (12)$$

Analysis of equation (11) shows that from the technological point of view, the possibility of realization of the process of capsule formation is excluded. This is explained by the fact that milk with a low content of ionic calcium (4–10 mg %) does not meet to the conditions of structuring by its concentration, and the rate of conversion of AlgNa to $\mathrm{Alg_2Ca_{Lac}}$ will be very low.

In this case, the kinetic equation of sodium alginate conversions can be described by dependence (11). It is evident that the rate of conversion of sodium alginate $-\frac{d[A\lg Na]}{d\tau}$ in this case will completely depend on the rate of the Ca^{2+}_{Lac}. ion accumulation.

The accumulation process is low-dynamic for milk (pH=7.0) (Fig. 2). Therefore, despite the general high content of calcium in its composition, milk cannot be used to realize the innovative idea of obtaining an encapsulated dairy product without additional technological influences. At the same time, when pH values of milk are reduced, the accumulation intensity increases.

From the thermodynamic point of view, accumulation of calcium ions is characterized by a significant increase in entropy in the technological system, therefore the change in the free energy of the system in this case is $\Delta G<0$. The process of transition of salts of dairy products from insoluble to ionized state depending on pH value is an entropy process ($\Delta S>0$) and is characterized by a limited solubility ($\Delta H<T\Delta S$). Restrictions occur at reaching the limit level of hydration of salt micelles under the given conditions and are characterized by the pH value and the type of acids which ensure transition of the calcium quantity characteristic of the given conditions to the ionic state. In a steady state, when the value of free entropy ΔG does not change which occurs at fixed pH values, self-dissolving of salts does not occur. At a dropping pH, solubility and hence temporary hydration of individual salts grow, non-equilibrium of concentrations in the solvent disappears with formation of a single-phase homogeneous thermodynamically equilibrium system of true solution.

If the conditions for dissolution have been created due to achievement of certain pH values, then dissolution of the micellar salts proceeds arbitrarily ($\Delta G<0$), that is, because of existence of actual concentration imbalance, the salt ion will spontaneously go over to a solvent with a lower chemical potential. When an equilibrium of concentrations occurs, i. e. $\frac{d\mu_i}{dc}=0$, saturation of the technological system with calcium ions stops (Fig. 2).

It is evident that kinetics of accumulation of free Ca^{2+}_{Lac} depends not only on pH values but also on the type of acid that is a donor $[\mathrm{H}^+]$. Therefore, concentration of Ca^{2+}_{Lac} ions will depend on the technological factors that bring about a change in pH which will make it possible to choose direction and adjust the rate of processing of milk and dairy products.

The calculations made according to expressions (7), (10) show that the minimum concentration of calcium ions for realization of the process of encapsulation in the "milk" system should be not less than 20–25 mg %. Since it is unlikely to accurately calculate the Ca^{2+}_{Lac} concentration during milk transformation with pH change, it is more appropriate to use whey which is an active donor of calcium ions as a source of the Ca^{2+}_{Lac}.

Indeed, sodium alginate is a salt formed by strong alkali (NaOH) and weak alginic acid. Under these conditions, joining of whey (as a source of the Ca^{2+}_{Lac} ions) and sodium alginate (as a source of Na^+ ions) is an energy-efficient reaction of substitution (displacement) of Na^+ for Ca^{2+}_{Lac} by the principle of the lyotropic series and can be used to form the calcium alginate gel. From the point of view of ensuring the technological process, the "whey" system should be given the function of encapsulant and the solution of sodium alginate should be given the function of an uninterrupted recepient medium into which encapsulant will be dropped. At the same time, the substitution reaction (from the colloidal point of view, the process of formation of calcium alginate gel) can be used as a basis for a fundamentally new technological process of preparation of encapsulated food products based on whey. Under these conditions, the functional role of whey is reduced to providing potentials to Ca^{2+}_{Lac} as a blocking electrolyte in reactions with a coordination bond or in substitution reactions. It is evident that whey can be used as an independent source of calcium ions and as a source of Ca^{2+}_{Lac} enrichment in a mixture with other nutrients (the "milk" system)

This is an important, fundamentally new interpretation since blending milk and whey with emergence of a new "milk-whey" system with a necessary level of ion concentration will not affect the colloidal stability of milk. On the other hand, it will provide the "milk" system with a highly effective potential in a form of Ca^{2+}_{Lac} ions that will effectively realize the process of its encapsulation. This opens up fundamentally new opportunities for milk processing with obtaining of products of high quality with new technological capabilities.

From the system point of view, the open technological "milk" system can be transformed into a "milk-whey" system with a limited openness in the encapsulated form. This, accordingly, ensures reducing of the effects of perturbing factors, that is, increasing controllability of the technological processes.

Thus, during modeling of the encapsulation process, a technological opportunity appears to instantly create the state of the system which by Ca^{2+}_{Lac} content will ensure realization of the forming process. This is realized by connecting partial units of the "milk" and "whey" systems in which the ratio of all forms of calcium will be clearly calculated and less pH dependent.

This approach is based on that the "whey" system can act as a donor of calcium ions. At the same time, the buffer capacity of the 'milk' system is sufficient to neutralize acidic pH values of whey with obtaining of a new technological "milk-whey" system. In this system, concentration of calcium ions is independent (within certain limits) of the values of the system pH. Fig. 3 shows a change in calcium concentration in the process of transformation of the "milk-whey" system in which whey is taken as the second component with a ratio of 0:100–100:0.

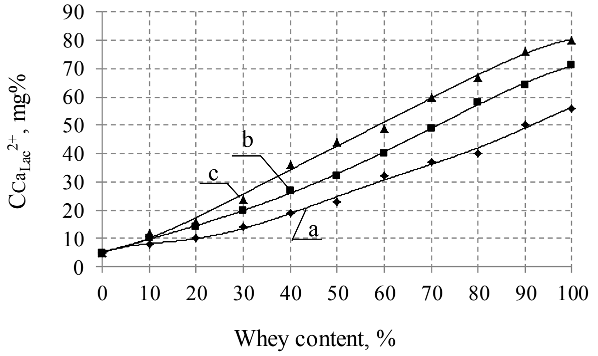

Fig. 3. The change of concentration of calcium ions depending on whey content in the "milk-whey" system at whey pH: 5.5 (a); 4.5 (b); 4.0 (c)

It is seen from the experimental curves that a technological possibility of a broader correction of the original technological "milk" system and hence controllability of technological processes is obtained.

From the point of view of planning and realization of the technologies for obtaining encapsulated dairy products, two possible situations are possible. They arise from the understanding of adequacy of ionic calcium as a carrier of chemical potential in an encapsulant. Formalized records of these situations which serve as the basis for calculation of the product composition and planning quality of end products, are as follows.

1. In the technology of encapsulated dairy products, such a concentration of sodium alginate is used which will ensure its quantitative excess respective to calcium by stoichiometric correlation. Then:

$$\begin{aligned}&(A^{-}\cdot b^{+})_n+[B^{+}_{Lac}+(B^{+}_{1Lac}\cdot a^{-}_1)+\\&+(B^{+}_{2Lac}\cdot a^{-}_2)]\xrightarrow{k_1\,(\mathrm{pH}\geq 5.0)}\xleftarrow[k_2,k_3,k_4]{}\\&[(\mathrm{A}^{-}\cdot b^{+})_x-(A^{-}\cdot B^{+}_{Lac}\cdot B^{+}_{1Lac}\cdot B^{+}_{2Lac})_y]+\\&+(n-x)(\mathrm{a}^{-}_1+a^{-}_2).\end{aligned}\tag{13}$$

In these conditions, from a technological point of view, an encapsulated product is obtained. From the point of view of thermodynamic characteristics, a system with the highest entropy level arises due to the absence of free (ionic) calcium and donor salts for its formation $[B^{+}_{Lac}+(B^{+}_{1Lac}\cdot a^{-}_1)+(B^{+}_{2Lac}\cdot a^{-}_2)]$. In this case, the excess sodium alginate $[(\mathrm{A}^{-}\cdot b^{+})_x-(A^{-}\cdot B^{+}_{Lac}\cdot B^{+}_{1Lac}\cdot B^{+}_{2Lac})_y]$ is characterized by a low chemical potential but it is not capable to affect the technological and thermodynamic stability of the final products. At such a composition, the capsule shell will be characterized by low permeability both from the side of the encapsulant and the side of environment and vice versa.

2. In the technology of encapsulated products, the process medium, i.e. whey in a form of encapsulant has a quantitative excess of calcium ions by concentration and is characterized by the presence of calcium ion donor salts. Then the scheme of interaction with the solution of sodium alginate will take the form:

$$\begin{aligned}&(A^{-}\cdot b^{+})_n+[B^{+}_{Lac}+(B^{+}_{1Lac}\cdot a^{-}_1)_x+\\&+(B^{+}_{2Lac}\cdot a^{-}_2)_y]\xrightarrow{k_1\,(\mathrm{pH}\leq 5.0)}\xleftarrow[k_2,k_3,k_4]{}\\&[(\mathrm{A}^{-}\cdot B^{+}_{Lac}\cdot(B^{+}_{1Lac})_{n-x}\cdot(B^{+}_{2Lac})_{n-y}]+\\&+(B^{+}_{1Lac}\cdot a^{-}_1)_{x-n}+(B^{+}_{2Lac}\cdot \mathrm{a}^{-}_2)_{y-n}+\\&(x-n)\cdot a_1+(y-n)\cdot \mathrm{a}_2+n\cdot b^{-}.\end{aligned}\tag{14}$$

It can be predicted from analysis of the reaction equation (14) that the process of capsule formation will feature high dynamics at a sufficient quantity of ionic calcium. At the same time, despite the presence of a chemical potential in the system in a form of a concentration excess of calcium ions $(B^{+}_{1Lac}\cdot a^{-}_1)_{x-n}+(B^{+}_{2Lac}\cdot \mathrm{a}^{-}_2)_{y-n}$ and a significant concentration of anti-ions (of anionic nature), there are no driving forces to remove the system from equilibrium at the existing pH values. Proceeding from the features of the calcium alginate gel, the capsule walls will be characterized by porosity and anisotropy.

6. Discussion of results obtained in developing the technological solutions for milk processing by encapsulation

One of the important characteristics enabling control of the encapsulation process is the form of obtained capsules. Geometric form of the obtained capsules must meet conditions of the form factor (K_f). Provided $K_f\approx 1$, the capsules will have a spherical form and if $K_f<1$, they will be close to an oval form (Table 1).

Table 1

Capsule forming capability and the form factor of the "milk-whey" systems

Milk:whey ratio	Content of Ca^{2+}_{Lac} mg %	Capsule forming capability	Form factor (K_f)
100:0	5.0	–	–
90:10	12.0	±	0.5
80:20	16.0	±	0.8
70:30	24.0	+	0.9
60:40	32.0	++	0.95
50:50	44.0	+++	1.0
40:60	49.0	+++	1.0
30:70	56.0	+++	1.0
20:80	67.0	+++	1.0
10:90	76.0	+++	1.0
0:100	80.0	+++	1.0

It is evident from Table 1 that the gradual growth of the whey fraction in the "milk-whey" system leads to a systematic increase in the content of ionized calcium. The "milk" system is characterized by Ca^{2+}_{Lac} content of 5.0 mg % and the respective figure for the "whey" system is 80.0 mg %. Blending of these systems makes it possible to obtain a new technological system with a well-calculated Ca^{2+}_{Lac} content. It should also be noted that the encapsulation ability in such systems appears only when the minimum required concentration of 24–25 mg % is reached. This is confirmed by the indicator of form factor which is 1 for the given values of Ca^{2+}_{Lac} content (Fig. 4).

Thus, it should be noted that blending of the "milk" and "whey" systems at a ratio of 70:30 is a prerequisite for accumulation of a critical concentration of ionic calcium (24–25 mg %) which ensures obtaining of encapsulated products with a regular spherical form. At the same time, such a ratio of components does not significantly alter the blend pH which is also an important criterion for realization of the encapsulation process.

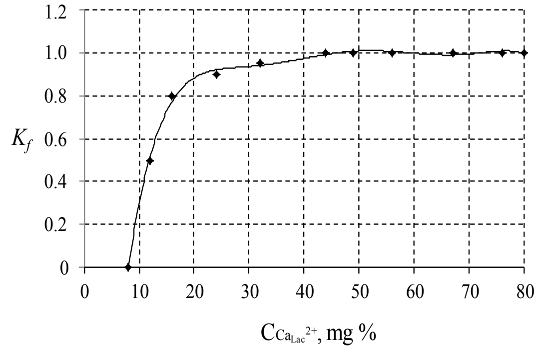

Fig. 4. Dependence of the form factor of capsules on Ca^{2+}_{Lac} content

At the next stage, a model of the technological system for milk processing by means of encapsulation was developed (Fig. 5).

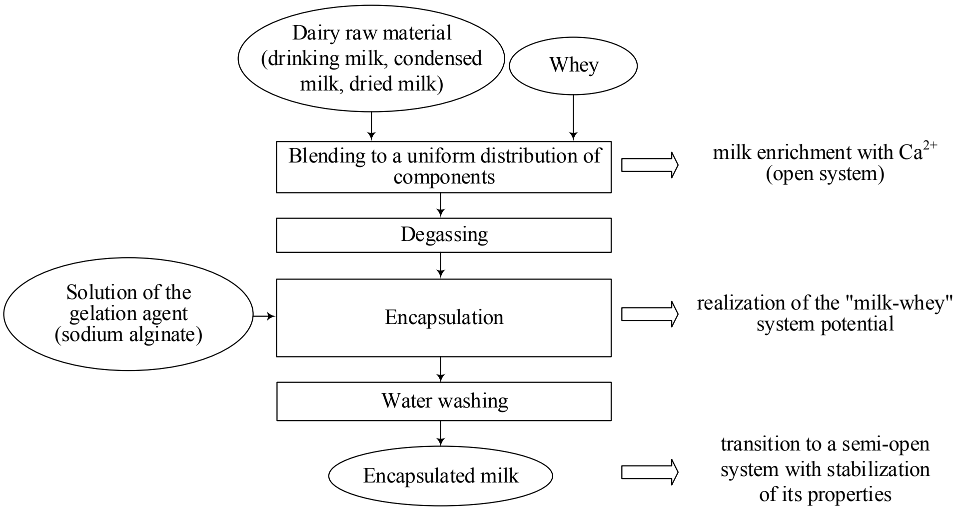

Fig. 5. Model of the technological system of milk processing by encapsulation

The process of encapsulating dairy raw materials can be conditionally divided into three stages. At the first stage, the “milk-whey” system is formed which due to its physical and chemical characteristics and thermodynamic potentials has the most favorable condition for realization of the encapsulation process. At the second stage (in the process of encapsulation), realization of the mentioned potentials takes place. Transition from the second to the third stage results in new technological forms of milk, namely capsules, which are semi-closed systems not capable of significant phase stratification with a pronounced syneresis.

Summarizing of the study results allows us to consider the “milk” system as a substance that can significantly change its potentials and hence the enthalpy/entropy ratio. This has made it possible to formulate new principles of stabilizing the “milk” system properties. In this case, determination of the laws of emergence of new potentials allows us to consider the possibility of its use in fundamentally new technologies which are based on the realization of these potentials in interaction with other substances. First of all, this refers to the interaction with ionotropic polysaccharides, e.g. sodium alginate which has a pronounced colloidal sensitivity to free calcium ions.

The undoubted advantage of the proposed technology is increase in the resource potential of dairy raw materials by involving secondary dairy raw materials (whey) to the workflow. It is also important to elucidate prospects of this study development taking into consideration possible ways of further processing of the resulting products.

It is evident that processing of such a system into a sour-milk product is more energy-efficient since the latter does not require accumulation of calcium ions. It follows from this that for obtaining sour milk products, it is more technologically suitable, requires less technological time, moves the material balance towards preservation of milk carbohydrates (lactose, galactose, glucose). This will improve organoleptic indicators and nutritional value of the products. The elucidated principles necessitate further studies of bacterial fermentation of such systems. It is also necessary to study the influence of temperature factors (pasteurization, freezing, defrosting, etc.) on the functional, technological and consumer properties of the new products.

Thus, the conducted studies have allowed us to develop the technology of milk processing with the use of secondary dairy raw materials. It is based on the realization of potentials of ionic calcium in dairy products. The developed approaches reveal the possibility of obtaining new dairy products in a form of capsules or granules.

However, it should be noted that one of the limiting factors of the proposed technological solutions is the strict control of calcium content in dairy raw materials and creation of conditions for its transition to the ionic state. The main problem is that the chemical composition of dairy raw materials, in particular the content of calcium, depends on many factors that cannot be controlled by food producers: breeds of cows, season, fodder type, etc. This can bring about variation of calcium content in dairy raw materials in a range of 100–140 mg %. As this factor is decisive in the technology of encapsulated products, it will necessitate applying of express analysis of dairy raw materials for the content of ionic calcium and developing corrective actions in the case of its insufficient quantity.

7. Conclusions

1. A working hypothesis was formulated the essence of which is the development of technological principles of the use of secondary dairy raw materials (whey) as carriers of chemical potentials in a form of ionic calcium. This makes it possible to effectively transform the dairy raw material into the dairy products fundamentally new in their composition and form.

2. Milk and sour milk products were studied in terms of defining of thermodynamic potentials. It has been established that milk has a pronounced potential for transformation of sodium alginate according to the “sol-gel

transition" scheme. However, this potential is ineffective and formation of capsules is only possible after its realization in an algorithm of the substantiated technological process. It is also obvious that whey can be used as an independent source of calcium ions and in a mixture with other nutrients (the "milk" system) as a source of their enrichment

3. Conditions of realization of the process of the "milk-whey" system encapsulation were studied. It has been determined that the "whey" system can act as a donor of calcium ions. At the same time, the buffer capacity of the "milk" system is sufficient to neutralize acidic pH values of whey to obtain a new technological "milk-whey" system in which concentration of calcium ions is sufficient for realization of the encapsulation process.

4. It was experimentally confirmed that blending of "milk" and "whey" systems in a ratio of 70:30 is a prerequisite for accumulation of a critical concentration of ionic calcium (24–25 mg %). This ensures obtaining of encapsulated products with a regular spherical form and the form factor equal to one. At the same time, such a ratio of components does not significantly change the blend pH which is also an important criterion for realization of the encapsulation process.

References

1. Engineering aspects of milk and dairy products / J. S. dos Reis Coimbra, J. A. Teixeira (Eds.). CRC Press, 2009. 275 p. doi: 10.1201/9781420090390
2. Analityka molochnoho rynku vid UFEB. URL: http://agronews.ua/node/75815
3. Spreer E. Milk and dairy product technology. Routledge, 2017. 483 p. doi: 10.1201/9780203747162
4. Niir B. Modern Technology Of Milk Processing & Dairy Products. 4th Ed. NIIR PROJECT CONSULTANCY SERVICES, 2013. 550 p.
5. Tanashchuk S., Savchenko O., Nikolaichuk A. Zastosuvannia ionoobminnykh smol // Kharchova i pererobna promyslovist. 2006. Issue 2. P. 23–25.
6. Donskaya G. A., Tihomirov G. P. Ispol'zovanie ionnoobmennyh processov dlya regulirovaniya sostava i svoystv molochnogo syr'ya i polucheniya ekologicheski chistoy produkcii // Pererabotka moloka. 2004. Issue 9. P. 27–29.
7. Assessing performance of skim milk ultrafiltration by using technical parameters / Rinaldoni A. N., Tarazaga C. C., Campderrós M. E., Padilla A. P. // Journal of Food Engineering. 2009. Vol. 92, Issue 2. P. 226–232. doi: 10.1016/j.jfoodeng.2008.11.009
8. Ultrafiltration in Food Processing Industry: Review on Application, Membrane Fouling, and Fouling Control / Mohammad A. W., Ng C. Y., Lim Y. P., Ng G. H. // Food and Bioprocess Technology. 2012. Vol. 5, Issue 4. P. 1143–1156. doi: 10.1007/s11947-012-0806-9
9. Chaharovskyi O. P., Didukh N. A., Didukh H. V. Kharchova ta biolohichna tsinnist pytnykh molochnykh napoiv herodietychnoho pryznachennia // Naukovi pratsi ONAKhT. 2007. Vol. 2, Issue 31. P. 144–150.
10. Bhat Z. F., Bhat H. Milk and Dairy Products as Functional Foods: A Review // International Journal of Dairy Science. 2011. Vol. 6, Issue 1. P. 1–12. doi: 10.3923/ijds.2011.1.12
11. Functional Dairy Products / Ortiz Y., García-Amézquita E., Acosta C. H., Sepúlveda D. R. // Global Food Security and Wellness. 2017. P. 67–103. doi: 10.1007/978-1-4939-6496-3_5
12. Yildiz F. Development and manufacture of yogurt and other functional dairy products. CRC press, 2009. 451 p. doi: 10.1201/9781420082081
13. Probiotic Dairy Products as Functional Foods / Granato D., Branco G. F., Cruz A. G., Faria J. de A. F., Shah N. P. // Comprehensive Reviews in Food Science and Food Safety. 2010. Vol. 9, Issue 5. P. 455–470. doi: 10.1111/j.1541-4337.2010.00120.x
14. Assessment of novel probiotic Lactobacillus casei strains for the production of functional dairy foods / Bertazzoni Minelli E., Benini A., Marzotto M., Sbarbati A., Ruzzenente O., Ferrario R. et. al. // International Dairy Journal. 2004. Vol. 14, Issue 8. P. 723–736. doi: 10.1016/j.idairyj.2004.01.007
15. Grynchenko N., Pyvovarov P. Development of technological decisions on production of capsulated products based on dairy raw materials // EUREKA: Life Sciences. 2018. Issue 3. P. 18–24. doi: 10.21303/2504-5695.2018.00659
16. Opisanie neravnovesnyh processov v energeticheskih zadachah metodami ravnovesnoy termodinamiki / Kaganovich B. M., Keyko A. V., Shamanskiy V. A., Shirkalin I. A. // Izvestiya Rossiyskoy akademii nauk. Energetika. 2006. Issue 3. P. 64–75.
17. Lewis M. J. The measurement and significance of ionic calcium in milk – A review // International Journal of Dairy Technology. 2010. Vol. 64, Issue 1. P. 1–13. doi: 10.1111/j.1471-0307.2010.00639.x