UDC 637.04:637.3
DOI: 10.15587/1729-4061.2017.117136

STUDY OF QUALITY INDICATORS OF FERMENTED-MILK CHEESE OBTAINED FROM SKIMMED MILK AT A CONTROLLED CONTENT OF CALCIUM

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Узагальнено результати досліджень щодо впливу вмісту кальцію у молоці знежиреному на його органолептичні, фізико-хімічні та технологічні властивості. Розглянуто можливість регулювання вмісту кальцію у молоці шляхом використання альгінату натрію. Визначено вплив процесу декальцифікації молока на якісні показники сиру кисломолочного, його мікроструктуру та дисперсність білкових часточок

Ключові слова: молоко знежирене, регульований вміст кальцію, декальцифікація, альгінат натрію, сир кисломолочний, казеїнові міцели, мікроструктура, дисперсність

Обобщены результаты исследований, связанные с влиянием содержания кальция в обезжиренном молоке на его органолептические, физико-химические и технологические свойства. Рассмотрена возможность регулирования содержания кальция в молоке путем использования альгината натрия. Определено влияние процесса декальцификации молока на качественные показатели творога, его микроструктуру и дисперсность белковых частиц

Ключевые слова: молоко обезжиренное, регулируемое содержание кальция, декальцификация, альгинат натрия, творог, казеиновые мицеллы, микроструктура, дисперсность

1. Introduction

Milk and products of its processing are both products of everyday demand and raw materials for many branches of the food industry in the national economies of Ukraine and the European Union member countries. Today, food manufacturers and consumers use different evaluation criteria. For consumers, it is a certain set of benefits (tangible and intangible) that meet their needs, lifestyle, desires, habits, traditions. Product freshness and undoubted benefits to health, long-term storage, practical and easy to use packaging are important characteristics for consumers. Also, flavor characteristics, which, to a certain extent, reflect physical, physical-chemical, structural, and mechanical properties of the product become determining characteristics. Completely different characteristics determined by the parameters of specific process operations are coming to the forefront for manufacturers on their way to achievement of required indicators. These characteristics define the relationship between an aggregate of technological effects (chemical, biochemical, thermal, hydromechanical, biological) and reaction of raw materials, semi-finished and finished products to these effects.

Regarding milk, one of the main requirements to it is suitability for processing which means its technological properties and safety indicators for obtaining high-quality dairy products. In present-day technical literature, technological properties of milk [1, 2] are considered the properties which ensure rational management of the technological process and the possibility of obtaining dairy products with prescribed composition and characteristics. Along with such indicators as absence of foreign substances, somatic cells, immune bodies in milk, other properties are important. For fermented-milk drinks, it is ability of milk to become sour and form clots with certain physical-chemical, structural, and mechanical characteristics. For canned dairy products, it is heat resistance of milk in the conditions of long-term heat treatment. For cream butter, it is the properties of triglycerides of milk fat to form a plastic and solid consistency. In the ice-cream technology, milk ability of whipping and withstanding freezing is important. Implementation of the technology for production of fermented-milk cheese requires raw materials with a high capacity of acid or maw coagulation. To date, the technological process of producing fermented-milk cheese based on classical technologies (acid coagulation) does not ensure final products with standardized high-quality indicators. The analysis of information sources [3, 4] and the experience gained by producers indicate that the main factors controlled in a raw material are protein and fat content, temperature and duration of milk pasteurization and the leaven properties. The process passing and the time of its end are determined by duration and temperature of fermentation and the active acidity of the leavened clot. However, an important role in this process is played by calcium, the content of which, above all, is associated with the end-product yield.

However, the initial value of calcium content in the raw material and its accumulation in the process of fermentation is a no less important factor influencing quality of the end-product. This indicator has a qualitative effect on both the size and structure of casein micelles and the total surface charge. During the technological process, the above factors manifest themselves by indicators of moisture-retaining ability of fermented-milk cheese and its dispersion.

Therefore, it is relevant to date to study relationship between the initial content of calcium in milk as a raw material for production of fermented-milk cheese and its end quality indicators.

2. Literature review and problem statement

Fermented-milk cheese is a protein product containing a biologically valuable protein (13.0–18.0 %), milk fat (0.5–18 %), milk sugar (1.0–1.5 %). Mineral substances (1.0–1.2 %) are represented by sodium (41–44 mg/100 g), potassium (112–116 mg/100 g), calcium (150–170 mg/100 g), phosphorus (220–224 mg/100 g), iron (0.3–0.4 mg/100 g), magnesium (22–25 mg/100 g). Vitamins A, B_1, B_2, B_6, B_{12}, PP are also identified. The food value is 90–230 kcal/100 g depending on the fat content [5].

From the point of view of production of fermented-milk cheese, protein (up to 3.6 %) is the most important component of which 80 % comes from casein. The remaining fractions of proteins are represented by albumin (0.5–0.8 %), globulin, and other proteins. According to [6], casein content is the main factor affecting milk suitability for making cheese and the yield of cheese. Casein in milk is in a form of micelles which are composite complexes of casein fractions with colloidal calcium phosphate. By its structure, the casein micelle consists of 10–20 nm diameter submicelles. Casein submicelles are interconnected by colloidal calcium phosphate, calcium citrate, hydrophobic bonds consisting of negatively charged groups and positively charged calcium ions. Hydrophilic groups bind water molecules forming a hydrate membrane that ensures stability of the casein micelle in fresh milk at pH 6.6 [7].

In milk, about 22 % of total calcium is tightly tied with casein, the rest is represented by salts: phosphates and citrates in colloidal and ion-molecular solutions. Equilibrium is established between various forms of calcium salts in milk. During heat treatment of milk, the balance of calcium phosphate forms becomes upset: some of the calcium hydrophosphates and dihydrophosphates that are in an ion-molecular form are transformed into poorly soluble calcium phosphate:

$$3CaHPO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + H_3PO_4,$$

$$3Ca(H_2PO_4)_2 \rightarrow Ca_3(PO_4)_2 \downarrow + 4H_3PO_4.$$

The formed calcium phosphate in a form of colloids is deposited on the surface of casein micelles resulting in an irreversible mineralization of caseinate-calcium-phosphate complex (CCPC) [8].

Fermented-milk cheese is a highly concentrated structured polydisperse system. The disperse phase of this system is formed by proteins and milk fat. The disperse medium is represented by an ion-molecular solution of lactose, some nitrogenous substances, mineral salts, organic acids, and other compounds [9]. The necessary stage of production of fermented-milk cheese is destabilization of the colloidal milk phase and its separation from the part of the dispersion medium. To achieve coagulation of the casein micelles, it is necessary to bring the system closer to the isoelectric point and destroy the stabilizing layer of the hydrate shell.

When producing fermented-milk cheese, one of the most important technological properties of milk is its ability to coagulate under the action of acid or maw. They determine rate of protein coagulation, density of the resulting clots, treatability and synergetic properties governing quality and yield of cheese [10]. As is known, acidic and maw coagulation of milk is the ability of its proteins to coagulate under the action of introduced leavening fermented-milk bacteria or a maw enzyme. The result of this process is formation of a dense clot which well separates whey and retains fat. The ability of milk to acidic and maw coagulation is determined by many factors. The main of these are the protein content (mainly casein) in milk, the degree of proteolysis and concentration of calcium salts (calcium ions) [11]. For making cheese with an optimal amount of proteins, their content should be not less than 3.2 %, in particular casein not less than 2.5 % [12].

The amount of calcium in cow's milk varies from 100 to 140 mg %. For cheese-making, content of calcium salts in milk within 125–130 mg % (including more than 8 mg % ionic calcium) is considered optimum [13]. The role of calcium ions in clot formation consists in that they carry out cross-links between casein micelles through the phosphoserile residues of casein. Papers [14–16] note that positively charged calcium ions neutralize surface charge and therefore contribute to reduction of the hydrated layer which partially retains paracasein micelles. Some researchers believe that when the casein concentration in milk is normal (at least 3.2 %), presence of colloidal calcium phosphate is necessary to form a clot. Otherwise, only formation of amorphous and loose flocculates occurs. Probably, colloidal calcium phosphate (CCP) plays an important role in the maw and acidic coagulation of milk: reduction of its content in casein micelles decreases the rate of micellar aggregation. With a decrease in the CCP by more than 20 %, no coagulation occurs at all unless an increased Ca ion content in milk is provided [14–16].

Thus, the content of ionic and colloidal calcium phosphate has a definite effect on density of the resulting acidic and maw clots and the product yield in cheese making.

Paper [17] notes that ionized calcium is accumulated in conditions of decreasing pH level. Ionized calcium is released from calcium-containing salts of the colloidal phase and participates in coagulation of milk proteins. There is a reference in literature [18, 19] to the fact that removal of ionized calcium from the system or its transfer from the ionized state to calcium-containing compounds regulates the technological properties of milk and milk-based products. Scientists [20, 21] proposed chemical and physical methods for regulating calcium content in milk which influences stability of its colloidal phase under the action of technological factors (active acidity, temperature). One of the promising methods is the ion exchange method which is realized in practice both by the use of ion exchange materials (ion exchangers) and introduction of stabilizer salts [22, 23]. However, the latter change chemical composition of milk. Proceeding from this, the question arises of the search for and introduction of more effective methods of ion exchange with the use of substances that can be removed from milk after the process completion.

The conducted analytical studies have shown expediency of using sodium alginate as an ion exchanger [24, 25]. Interaction of sodium alginate and free calcium ions of milk results in formation of a gel in a form of globular granules. As a result of the ion exchange reaction, sodium alginate turns into calcium alginate which has a gel-like structure. The obtained granules can be extracted from skimmed milk with a simultaneous decrease in calcium content in it.

Analysis of the above data indicates that the main studies of the relationship between calcium and milk proteins lie in the plane of determining effect of the mineral composition of milk on the caseinate-calcium-phosphate complex stability. It should be noted that we did not find systematic studies conducted to establish the effect of calcium content in milk on quality of fermented-milk cheese with a regulated calcium content. Therefore, the issue of determining the correlation between calcium content in milk and quality of fermented-milk cheese made on its basis is a topical issue. It is easy to predict that regulation of the initial calcium content in skimmed milk will have a significant effect on quality of fermented-milk cheese. Specifically, its texture, plasticity, moisture-retaining ability will change. In addition, the fixed content of calcium in the raw materials will enable obtaining of the end products with consistent quality indicators and determine the target use of such raw materials in culinary and confectionery products.

3. The aim and objectives of the study

This work objective was to study the influence of the skimmed milk decalcification process on qualitative characteristics of fermented-milk cheese made on its basis. This will make it possible to obtain fermented-milk cheese with a reduced calcium content featuring high organoleptic indicators and stable physical-chemical characteristics.

To achieve this goal, the following tasks were addressed:

– determine organoleptic and physical-chemical parameters of milk with various calcium content as a technological system used for the production of fermented-milk cheese;

– study the change in organoleptic and physical-chemical properties of the fermented protein clot and whey obtained on the basis of skimmed milk with various calcium contents;

– determine correlation between the calcium content in the raw material and the organoleptic and technological properties of fermented-milk cheese.

4. Materials and methods used in the study of milk, acid clots, whey and fermented-milk cheese

The objects of the study were as follows:

– skimmed milk prepared by separating whole milk delivered from Kutuzivka State Enterprise of the National Academy of Sciences of Ukraine;

– complexing agent: sodium alginate (AlgNa) FD-157 (produced by Danisco Company) which is authorized for use by the Ukrainian Central Executive Body in the Sphere of Public Health;

– skimmed milk with various calcium contents achieved by sorption of ionized calcium with AlgNa solution;

– fermented-milk cheese obtained from skimmed milk with various calcium contents.

AlgNa solutions were prepared by dispersing weighted quantity of AlgNa in de-aerated and demineralized drinking water at a temperature of 18–20 °C for 3–4 to 60 sec followed by holding for $24 \cdot 60^2$ sec.

Sorption of ionic calcium was carried out by dropping the AlgNa solution into cow's milk followed by exposure for 1 hour to form a gel in a form of globular granules which were further removed by decantation (Fig. 1).

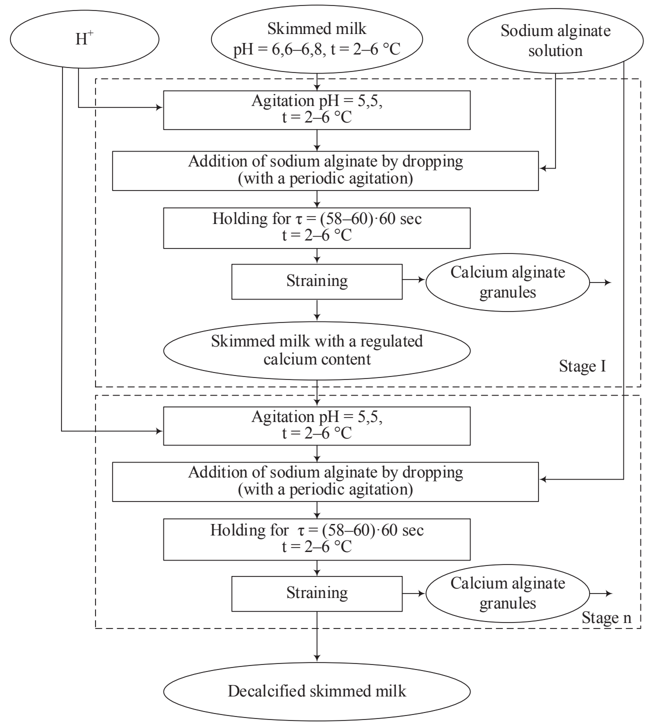

Fig. 1. Model of technological system of skimmed milk decalcification for the use of sodium alginate as a natural ion exchanger

Samples of fermented-milk cheese prepared from skimmed milk (control) and decalcified milk were obtained using the traditional technology by acidic method taking milk from the same batch. Milk was pasteurized at a temperature of 78·80 °C for 20–30 seconds and cooled to 32–34 °C. Leaven culture was added directly to the prepared milk and the thermostating was carried out at a temperature of 32–34 °C to a pH of 4.5–4.6. The resulting clot was cut into 2×2×2 cm cubes for better whey separation. To accelerate whey separation, the prepared clot was heat treated to a temperature of 40–42 °C for (15–30)·60 sec. Whey was separated from the boiled clot which was subjected to self-pressing at a temperature of 16–20 °C. The resulting clot was cooled to a temperature of 4–6 °C.

The following research methods were used during the experimental work.

The methods used in studying milk, acidic clots, whey, and fermented-milk cheese are given in [26].

4. 1. The methods used in milk study

The mass fraction of fat, protein, lactose and dry matter in milk for various Ca^{2+} contents was determined with the help of BENTLEY SOMACOUNT-150 (Bentley Instruments Inc., USA) (Fig. 2).

The mass fraction of total mineral matters and the skimmed milk mineral composition were determined using the X-ray fluorescence ElvaX Light SDD analyzer (Elvatex, Ukraine) (Fig. 3).

Fig. 2. BENTLEY SOMACOUNT-150 milk analyzer

Fig. 3. ElvaX Light SDD X-ray fluorescence analyzer

Calcium content in skimmed cow's milk and in decalcified cow's milk was determined by the method of complexometric titration. The method is based on the interaction of calcium with trilon B in an alkaline medium. The result of this reaction is transition of calcium from protein compounds and phosphorus into solution. The remainder of trilon B was titrated with a calcium chloride solution [27].

Active acidity of skimmed milk was determined using a pH-150 MI pH meter (Measurement Engineering, Russia) with an electrode system for measuring pH. Titrated acidity of milk and fermented-milk cheese was found by titration of samples with 0.1 N by sodium hydroxide solution. Titration was carried out in the presence of phenolphthalein until a steady faint pink color appeared during 60 sec.

4. 2. The methods used in the study of acidic clots and whey

The clot moisture release (CMR) ability of protein was determined by centrifugation at a separation factor of 1,000. The ability of clots to release moisture was judged by the amount of separated whey. The results were expressed in milliliters of whey derived from 10 cm^3 of acidic clot.

The weight portion of protein and dry matter in whey were determined with the help of BENTLEY SOMACOUNT-150 device (Bentley Instruments Inc., USA).

4. 3. The methods used in the study of fermented-milk cheese

The study of the total protein content in raw dairy products for various calcium content was carried out using the Kjeldahl method [28].

The moisture-retaining ability of fermented-milk cheese was determined gravimetrically. The method is based on determining the amount of water released from the product under a light compression and absorbed into filtering paper. The work was carried out using ashless, slowly absorbing 9–11 mm dia. filters which were kept in an exicator with calcium chloride to establish a constant moisture content. The filter was placed on a 11×11×0.5 cm glass plate. A weighed (0.3 g) portion of cheese was placed on a 40-mm dia. polyethylene film circle, weighed with an analytical balance to an accuracy of 0.5 mg and transferred to the filter so that the weighed portion was under the polyethylene circle. On top of the film, the weighed portion was covered with a glass plate of the same size and a load of 0.5 kg was put on it. The content was pressed for 5–7·60 sec. After that, the pressure filter together with the weighed portion was released from the load and plate. A sample of cheese together with a polyethylene circle was taken from the filter paper and weighed. The difference in the weight of the product with the circle before and after pressing shows the weight of moisture released from the sample. The water retaining capacity (MRC) was determined by formula (1).

$$MRC = 100 \cdot \frac{a-b}{a}, \qquad (1)$$

where MRC is moisture-retaining capacity of fermented-milk cheese, %; a is the amount of moisture in the weighed portion of cheese, g; b is the amount of moisture released from the weighed portion of cheese, g.

The amount of moisture in the weighed portion of cheese was determined by formula (2):

$$a = \frac{300 \cdot B_{FMC}}{100}, \qquad (2)$$

where 300 is weighed portion of cheese, mg; B_{FMC} is mass fraction of moisture in fermented-milk cheese, %.

The mass fraction of moisture in the studied systems was determined using the Infrared Moisture Meter, Model F-IA (Kett Electric Laboratory, Japan) (Fig. 4).

Fig. 4. Infrared Moisture Meter, Model F-IA (Kett Electric Laboratory)

The device action is based on the thermogravimetric principle: the moisture of the specimen under investigation is determined by the decrease in its weight as a result of drying during heating. As a heating element, infrared lamps were used.

The fermented-milk cheese microstructure was evaluated using a light microscope with a photo attachment for a 40-fold magnification. To prepare specimens in a mortar to a homogeneous mass, an average sample of fermented-milk cheese was ground. Next, 0.005 g of the material was evenly applied by a loop to the object-plate and microscoped randomly selecting the field of view over the entire surface of the material to obtain objective, statistically reliable results and photographed.

The fermented-milk cheese dispersion was determined using a microscope with a digital camera and a personal computer with a software for processing obtained photographs. The sample of the studied systems was photographed using a microscope and a digital camera. The resulting photographs were processed using the ImageJ 1.47 software by counting the number of particles and defining their diameter by formula (3):

$$d = 2\sqrt{S/\pi}, \qquad (3)$$

where S is the particle area.

Optical density of the fermented-milk cheese samples was measured on a CPC-2 (Russia) concentration photoelectron colorimeter. On the basis of the obtained data, sedimentation stability of the selected samples was determined. To prepare the samples, the weighed portion of fermented-milk cheese was ground in a mortar to a homogeneous mass and mixed with distilled water at a sample/water ratio of 1:500. Cuvettes with distilled water and the sample under study were placed in cuvette holders of the device. The wave length during measurement was 540 nm.

Organoleptic evaluation of the samples was carried out by sensory analysis [29].

Experimental studies were conducted in the following research laboratories:

– rheological research laboratory of Kharkiv National University of Food and Trade (Ukraine);

– laboratory for assessing fodder and livestock product quality of the Institute of Cattle-breeding of NAS of Ukraine;

– research laboratory of the Department of Organic Synthesis and Nanotechnologies of Kharkiv National University, Kharkiv Polytechnic Institute (Ukraine).

5. Results obtained in the studies of influence of the skimmed milk decalcification process on the fermented-milk cheese quality

Skimmed milk with various calcium contents was obtained by the way of milk sorption by a natural ion exchanger, sodium alginate. It has been proved that the use of sodium alginate as a sequestrant enables a 10 % to 55 % calcium removal from skimmed milk to its initial content. In addition, it considerably adjusts the technological properties of milk as a food system. First of all, changes occur in thermal and acid resistance of milk, dispersion of casein micelles, coagulation processes, etc.

Using ion exchange, skimmed milk was obtained with a low calcium content which was later used to produce fermented-milk cheese. To prepare samples of fermented-milk cheese, skimmed drinking milk (calcium content of 132–137 mg % in the control sample) and skimmed decalcified drinking milk were used. In decalcified milk, calcium content was reduced by 10–52 % compared with the control sample. In parallel, drinking skimmed milk with an addition of calcium chloride as a sedimentation agent was studied. This method is traditionally used in the industrial production of fermented-milk cheese (145–147 mg % calcium content).

The influence of calcium content in skimmed milk on its organoleptic, physical, physical-chemical parameters and mineral composition of ash residue (Table 1–3) was investigated.

Table 1

Organoleptic indicators of skimmed milk as a technological system for production of fermented-milk cheese

Indicator name	Characteristics of milk and calcium content in the system, mg % (decalcification degree)				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–95 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
Appearance and consistency	Homogeneous liquid with no sediments, protein flakes and fat lumps				
Taste and smell	Pure, with no unwanted aftertastes and smells peculiar to fresh milk, with a light pasteurization aftertaste				With a bitter metal aftertaste, with no unwanted smells
Color	White, uniform in the entire mass		White, uniform in the entire mass, glassy		White, uniform in the mass, with a bluish hue

Table 2

Physical-chemical indicators of skimmed milk as a technological system for obtaining fermented-milk cheese

Indicator name	Characteristics of milk and calcium content in the system, mg % (decalcification degree)				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–105 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
Weight fraction of dry matter, %	9.55±0.1	9.05±0.1	8.57±0.1	8.37±0.1	9.57±0.1
Weight fraction of protein, %	3.1±0.1	3.0±0.1	2.9±0.1	2.9±0.1	3.1±0.1
Including casein, %,	2.6±0.1	2.5±0.1	2.5±0.1	2.5±0.1	2.6±0.1
Weight fraction of fat, %	1.0±0.1	1.0±0.1	1.0±0.1	1.0±0.1	1.0±0.1
Weight fraction of lactose, %	4.7±0.1	4.3±0.1	3.9±0.1	3.7±0.1	4.7±0.1
Weight fraction of mineral substance, %	0.45±0.05	0.45±0.05	0.44±0.05	0.43±0.05	0.47±0.05
Titrated acidity, °T	20±1	21±1	21±1	21±1	21±1
Active acidity, pH units	6.6±0.1	6.4±0.1	6.2±0.1	6.0±0.1	6.5±0.1
Optical density	0.89	0.67	0.57	0.55	1.01

An analysis of the data given in Table 1, 2 makes it is possible to establish changes in organoleptic, physical and physical-chemical parameters of skimmed milk in correlation with calcium content. Taking into account the organoleptic characteristics, it is evident that appearance, consistency, taste and smell of milk do not change during decalcification. At the same time, removal of 20–52 % of calcium from the system results in a vitreous appearance (samples 3, 4). An increase in calcium content thru introduction of soluble $CaCl_2$ salts (sample 5) is accompanied by appearance of a bitter metallic taste and a bluish tint.

It has been experimentally established that during decalcification of skimmed milk, a decrease in the mass fraction of dry matter takes place: from 9.55±0.1 % (sample 1) to 8.37±0.1 % (sample 4). This is probably because of removal of compounds with a low molecular weight (lactose, soluble mineral salts, etc.) along with a complex of calcium alginate. The reduction in lactose content from 4.7±0.1 % (sample 1) to 3.7±0.1 % (sample 4) has been reliably established. The change in the content of other substances was within the measurement error. In a number of samples 1–4, an increase in titrated acidity (from 20±1 °T to 21±1 °T) and a decrease in the active acidity (from 6.6±0.1 to pH 6.0±0.1 pH units) was established. Reduced optical density of skimmed milk was found, probably because of decomposition of casein micelles which is fully consistent with its organoleptic parameters. Physical and physical-chemical parameters of skimmed milk with a high calcium content (sample 5) are identical to the control sample 1.

The changes in the content of the main trace elements in skimmed milk during decalcification and additional calcium introduction (Table 3) were investigated.

Table 3

Content of main microelements in skimmed milk as a technological system for making fermented-milk cheese

Indicator name	Content of mineral substances and main microelements in skimmed milk at calcium content in milk, mg % (decalcification degree)				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–105 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
Weight fraction of mineral substances, %	0.45±0.05	0.45±0.05	0.44±0.05	0.43±0.05	0.47±0.05
potassium, mg %	155±5	155±5	155±5	153±5	155±5
sodium, mg %	12±1	23±1	45±1	78±1	12±1
calcium, mg %	135±2	121±1	104±2	70±2	147±2
magnesium, mg %	12±1	13±1	15±1	15±1	11±1
phosphorus, mg %	35±1	35±1	36±1	36±1	36±1

It has been experimentally established that with a practically constant total content of mineral substances of 0.45–0.47 % during decalcification of skimmed milk, there was a significant decrease in calcium (from 135±2 mg % to 70±2 mg % in samples 1, 4). At the same time, the increase of sodium content (from 12±1 mg % to 78±1 mg %, respectively) was observed which resulted from ion-exchange reaction. Introduction of soluble $CaCl_2$ salt lead to a regular increase in calcium content to 147±2 mg %.

The next stage of the research was elucidation of the effect of calcium content in skimmed milk on the quality characteristics (organoleptic, physical, physical-chemical) and the yield of fermented-milk cheese.

Organoleptic estimation of the clot, whey and fermented-milk cheese was carried out in the process of production of fermented-milk cheese. The clot MRA, content of dry matter and protein in whey, acidity, moisture and yield of the fermented-milk cheese were monitored as well (Table 4–6).

Table 4

Physical-chemical and organoleptic indicators of whey and clots obtained from skimmed milk at various calcium content values in milk

Indicator name	Characteristics at calcium content in milk, mg % (the degree of decalcification)				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–105 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
Weight fraction of dry matter in whey, %	5.8±0.1	5.8±0.1	6.2±0.1	7.3±0.1	5.0±0.1
Weight fraction of soluble protein in whey, mg/cm^3	3.5±0.1	3.9±0.1	4.2±0.1	8.9±0.1	3.0±0.1
The clot CMR, ml of whey	3.0±0.1	2.5±0.1	2.4±0.1	2.0±0.1	5.8±0.1
Whey characteristics	Transparent, light green	Transparent, light green	Slightly turbid, white-greenish	Turbid, with protein dust	Transparent, light green
Clot characteristics	Dense, with a distinctive cleavage, well separates whey		Dense, slightly viscous	Flabby, badly separates whey	Dense

It has been experimentally established that the reduction of calcium content in skimmed milk influences the organoleptic and physical-chemical parameters of whey and clots as intermediate semi-finished products obtained in the technological process of producing fermented-milk cheese. It was found that with a decrease in the calcium content (in a number of samples 1–4), the content of dry matter in whey increases from 5.8 % to 7.3 % respectively. This is explained by decomposition of the casein micelle into small submicelles which remain in whey after the separation of cheese. This is confirmed by an increase in the weight fraction of soluble protein in whey. Also, appearance of protein powder (sample 4) and worsening of whey separation of (sample 4) were observed. Whey became muddy. On the contrary, when the content of dry matter including whey soluble protein decreased, clear whey and dense clots were observed when the calcium content in skimmed milk increased (sample 5).

Organoleptic and physical-chemical parameters, yield of fermented-milk cheese produced from skimmed milk at various calcium contents (Table 5, 6) were determined and the degree of applicability of dry milk substances were found by calculation.

Table 5

Organoleptic indicators of fermented-milk cheese obtained from skimmed milk at various calcium contents in milk

Indicator name	Characteristics of fermented-milk cheese at various calcium contents in milk mg % (the degree of calcification)				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–105 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
Consistency and appearance	Crumbly, with a distinct granularity. Minor whey separation	Spreadable; absence of crumbs; no whey separation		Spreadable, soft, with an insignificant amount of whey separation	Inhomogeneous, with a marked granularity and a significant amount of separated whey
Taste and smell	Characteristic sour milk taste, with no unwanted after-tastes and smells				Characteristic sour milk taste, with a bitter after-taste and smell with no unwanted smells
Color	White with a creamy hue, uniform in the entire mass				

Table 6

Physical-chemical indicators of fermented-milk cheese obtained from skimmed milk with various calcium contents in milk

Indicator name	Characteristic of fermented-milk cheese with various calcium contents in milk, mg % (the degree of calcification)				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–105 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
Weight fraction of moisture, %	75.3±0.1	75.7±0.1	76.8±0.1	67.6±0.1	74.9±0.1
Weight fraction of protein, %	16.5±0.1	16.0±0.1	16.0±0.1	15.2±0.1	17.1±0.1
pH	4.5	4.7	4.9	5.0	4.5
MRA, %	42.0±1.0	49.6±1.0	52.2±1.0	33.5±1.0	40.7±1.0
Yield, %	15.7±0.5	16.5±0,5	18.9±0.5	11.6±0.5	15.9±0.5
Degree of use of milk dry matter, %	55	54	54	46	58

Summarizing the study results given in Table 5, 6 makes it possible to reveal the following regularities: reduction of calcium content in skimmed milk at unchanged taste, smell and color significantly affects consistency and appearance of fermented-milk cheese. Control sample 1 was characterized by a crumby, granular consistency, with pronounced grains and a slight whey release. Specimens 2–4 featured a spreadable soft consistency, absence of crumbs and separation of whey. It was established that in a number of samples 1–3 there was an increased weight fraction of moisture and a slight decrease in the weight fraction of protein. It should be noted that the regularities of changes in MRA, the yield of fermented-milk cheese and the degree of use of milk dry matter are of a somewhat different (extreme) character. It was found that reduction of calcium content in skimmed milk by 10–25 % (samples 2, 3) resulted in a growth of MRA and yield. At the same time, extraction of calcium from milk in an amount of 45–52 % during decalcification (sample 4) significantly degraded the above-mentioned indicators. For sample 4, a characteristic reduction of MRA down to 33.5±1.0 % and yield down to 11.6±0.5 % was observed. The calculated indicator of the degree of use of dry milk matter completely correlated with the above-mentioned regularities.

In order to establish the effect of calcium content in skimmed milk on the properties of a dispersed system, such as fermented-milk cheese, a comparative analysis of microstructure and the disperse phase sizes in the control and experimental samples of the product was performed (Fig. 5).

It was found by microstructural studies that the structure of all samples consisted of the same structural elements, namely macro-grains with inclusions in a form of micro-grains separated from each other by fluid interlayers with macroscopic voids (capillaries). The latter determine structural properties of acid gels, i. e. porosity and permeability which depend on the size and the number of capillaries. This, in turn, affects the degree of synergy and the moisture-retaining capacity of the product. The presence of fluid interlayers between macro- and micro-grains resulted in a smaller structural strength but it imparted plasticity to the product: the larger the size and the number of interlayers, the lower strength of the structure.

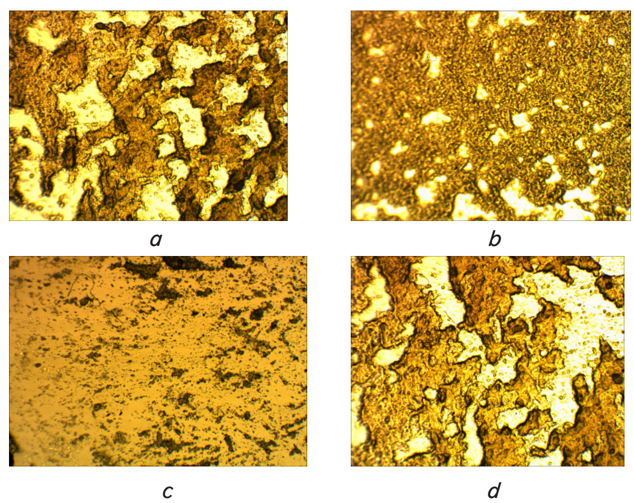

Fig. 5. Microstructure of fermented-milk cheese obtained from skimmed milk at calcium content in milk: *a* – 132–137 mg %; *b* – 90–123 mg %; *c* – 65–72 mg %; *d* – 145–147 mg %

The comparative microstructural analysis of the samples taken from fermented-milk cheese has made it possible to assert the differences in the nature of distribution of the dispersed phase in a form of conglomerates of protein particles and macro-voids in the control and experimental samples. For example, sample *a* (control sample) was characterized by a heterogeneous structure and contained well-visible micro-voids which essentially were capillaries. Reduction of calcium content in skimmed milk resulted in obtaining of fermented-milk cheese (samples *b, c*) with a more homogeneous finely-dispersed structure. Microstructure of the sample *c* did not contain interlayers and voids. It consisted of protein grains of the same shape uniformly distributed in the entire volume. Microstructural analysis of the specimen *d* has revealed a more pronounced agglomeration of protein macro-grains and presence of a large number of bigger micro-voids.

Fig. 6 shows microphotographs of the samples used in a quantitative assessment of fermented-milk cheese dispersion.

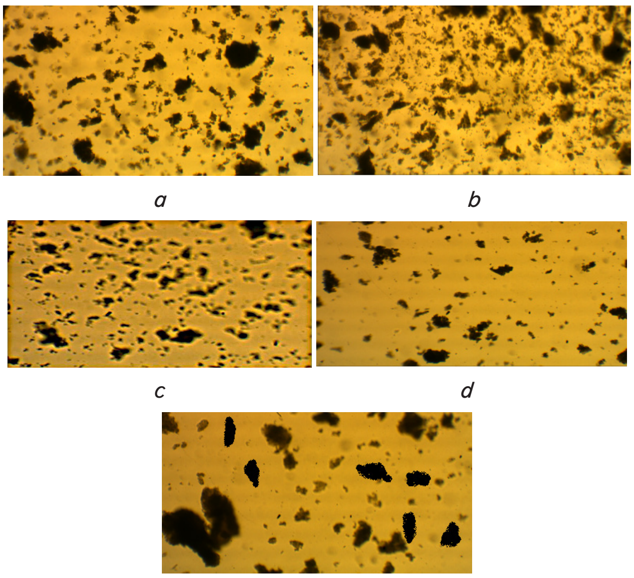

Fig. 6. Microphotographs of protein particles of fermented-milk cheese obtained from skimmed milk at calcium content in milk: *a* – 132–137 mg %; *b* – 118–123 mg %; *c* – 90–105 mg %; *d* – 65–72 mg %; *e* – 145–147 mg %

The summarized data on size distribution of protein particles are given in Table 7.

Table 7

Protein particle size distribution in fermented-milk cheese obtained from skimmed milk with various calcium contents in milk

Protein particle size (L), μm	Content of protein particles in samples of fermented-milk cheese with calcium contents in milk, mg % (the degree of decalcification), %				
	1 132–137 (control)	2 118–123 (10–12 %)	3 90–105 (20–25 %)	4 65–72 (45–52 %)	5 145–147 ($CaCl_2$ added)
≤10.0	13.3	22.3	36.7	40.1	5.7
10.0<L≤20.0	36.8	40.2	46.7	47.3	29.0
20.0<L≤30.0	33.3	24.4	7.6	7.5	32.5
30.0<L≤40.0	10.0	10.0	9.0	5.1	14.4
>40.0	6.6	3.1	–	–	18.4
Total	100.0	100.0	100.0	100.0	100.0

Analysis of the study data makes it possible to establish that the microstructure of the control sample 1 (Fig. 6, *a*) was represented predominantly by protein particles with an equivalent diameter of 10–30 μm make 70.1 %. The particles with a size less than 10.0 μm make 13.3 %. The rest (16.6 %) are particles with an equivalent diameter >30.0 μm. In samples of fermented-milk cheese made from skimmed milk with a reduced calcium content (Fig. 6, *b*–*d*), there was a redistribution of the equivalent diameter of protein particles towards growth of their dispersion. For example, samples 2 and 3 featured an increase in the weight fraction of protein particles with equivalent diameters of ≤10.0 μm up to 22.3 % and 36.7 %, respectively, a decrease in the weight fraction of protein particles with equivalent diameters of 20.0<L≤30.0 down to 24.4 and 7.6 %, respectively, and absence of particles with sizes >40.0 μm. Sample 4 was characterized by even higher dispersion and contained protein particles with an equivalent diameters ≤10.0 μm and 20.0<L≤30.0 which were predominant. It has been experimentally proved that the additional introduction of calcium into the system in a form of soluble $CaCl_2$ salt brought about a decrease in dispersion, formation of protein particles with a predominant equivalent diameter of 30 μm or more.

The results obtained in the study of sedimentation stability of protein particles also completely correlate with the results obtained in the study how calcium content effects their dimensional characteristics (Fig. 7).

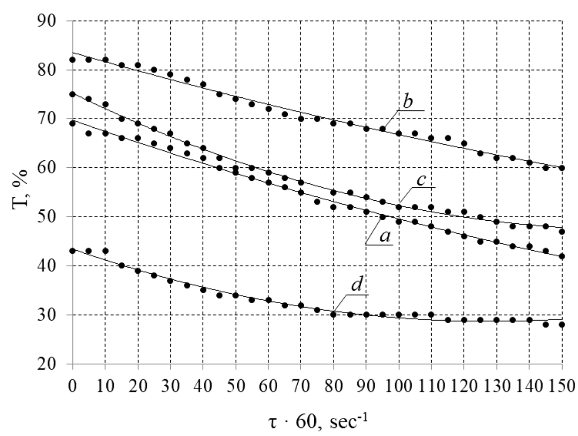

Fig. 7. Sedimentation stability of protein particles of fermented-milk cheese made from skimmed milk with the content of calcium in milk: 132–137 mg % (*a*); 90–123 mg % (*b*), 65–75 mg % (*c*), 145–147 mg % (*d*)

A direct relationship between the size of protein particles (Table 7) and the sedimentation stability of systems under study (Fig. 7) was revealed. It has been established that when calcium content is reduced resulting in a growth of the fraction of smaller particles, colloidal stability increased. This reduction of calcium content increases the system resistance to stratification. Thus, a decrease in calcium content increases sedimentation resistance by 1.4 times and an increase in the calcium content in the system leads to an opposite effect: a 1.5 times lower sedimentation stability compared to the control sample.

6. Discussion of the results obtained in the study of influence of calcium content on the qualitative indicators of fermented-milk cheese

The analysis of the data obtained in experiments makes it possible to conclude that regulation of calcium content in skimmed milk affects its organoleptic, physical and physical-chemical properties. In addition, the process of decalcification of milk largely determines the properties of fermented-milk cheese made on the basis of this milk.

The relationship between the properties of skimmed milk, clot and fermented-milk cheese prepared in the technological flow has been established. It has been experimentally proved that regulation of calcium content in skimmed milk (use of natural sodium alginate ion exchanger decreases and introduction of calcium chloride increases calcium content) allows producers to achieve various technological effects.

For example, generalization of the study results allows us to determine that it is rational to extract 20–25 % calcium to its initial value from skimmed milk as a technological system. Under these conditions, fermented-milk cheese is obtained which is characterized by a spreadable consistency and absence of crumbs and whey separation. The aforementioned sample of fermented-milk cheese compared with the control sample is characterized by 1.2 times higher MRA (52.2±1.0 % and 42.0±1.0 % respectively), a higher percentage of moisture (76.8±0.1 % and 75.3±0.1 % respectively), which increases yield of the end product by 16.9 %. It was also determined that a decrease in the mass fraction of dry matter (from 9.55±0.1 % to 8.57±0.1 %, respectively) was observed during decalcification of skimmed milk, mainly because of lactose content. However, it should be pointed out that at the same time the degree of use of dry milk matter is practically unchanged and measures 55 % and 54 %, respectively.

It was established that at the above-mentioned rational parameters of decalcification of skimmed milk, a homogeneous fine-grained structure of fermented-milk cheese without interlayers and voids was formed. This structure contained protein grains of the same shape which completely correlated with the dimensional characteristics of protein particles. It was confirmed that with a decrease in calcium content in milk, an increase in dispersion of casein fractions occurred, which brought about increase in the sedimentation stability of their aqueous dispersions.

From the scientific point of view, the results obtained in the study are promising in view of modification of casein micelles which consists in a destruction of caseinate-calcium-phosphate complex with a simultaneous break-up of the casein micelle to submicelles. From a practical point of view, implementation of the proposed technology with substantiated parameters allows producers to make fermented-milk cheese of a high dispersion, moisture-retaining capacity and a homogeneous structure. It also raises the product output that is economically grounded. The results obtained fully correlate with the fundamental study of the effect of binding calcium thru an ion-exchange processing on dissociation of casein micelles [18, 22]. The authors of these studies assert that the process of decalcification of milk and concentrates on its basis is accompanied by a growth of solubility of casein micelles and a change in their structure with improved functionality of the latter.

Interesting from scientific and practical points of view is disclosure of the results obtained in the field of non-rational (from the point of view of fermented-milk cheese production) parameters of decalcification of skimmed milk (samples 2, 4). For example, extraction from skimmed milk calcium in an amount of 10–12 % to the initial content results in obtaining of fermented-milk cheese which, according to organoleptic, physical and physical-chemical indicators, is close to the control sample. Sample 2 was characterized by a spreadable consistency, more homogeneous compared with the control sample, fine-grained structure, absence of crumbs, and whey separation. In the sample 2, an increase in MRA (from 42.0+1.0 % to 49.6+1.0 %) and yield (from 15.7±0.5 % to 16.5±0.5 %) was observed at close to the control sample 1 mass fraction of moisture and protein (Table 6). On the one hand, the interval of calcium content in sample 2 lies in the region close to the rational one considering the requirements to fermented-milk cheese and on the other hand it reflects the regularities of changes in the properties of food systems during decalcification.

Increase in the degree of milk decalcification more than rational values (sample 4) results in a significant deterioration of physical-chemical indicators of fermented-milk cheese. It is likely that because of the increased degree of dissociation of casein micelles, decrease in their molecular weight and increase in solubility, a decrease in the mass fraction of protein, decrease in MRA and yield of the end-product take place. In this case, uniformity of the structure without voids and interlayers was observed (Fig. 5, *c*). 87.4 % of the protein particles in sample 4 have an equivalent diameter ≤20.0 μm, which indicates a high dispersion of the latter (Table 7). Therefore, binding and elimination of more than 45 % calcium from the skimmed milk to its initial value is not rational from the point of view of production of fermented-milk cheese. At the same time, the obtained results open the prospects for using the decalcification process to obtain milk protein concentrates with new functional and technological properties: dispersion, solubility, emulsification capacity, etc.

It is important to note that the production of fermented-milk cheese from skimmed milk with a regulated calcium content allows producers to significantly expand its technological use in the production of food products by the food industry and restaurants. It is possible to predict its effective use in the technology of culinary and confectionery products where fermented-milk cheese is used as the main recipe component.

Thus, the applied aspect of implementation of the proposed technological solutions consists in increase of the resource potential of milk as a raw material, improvement of efficiency of the technological process, development of a wide range of competitive products with high consumer properties for various segments of population.

7. Conclusions

1. Regularities of changes in the organoleptic, physical and physical-chemical indicators of skimmed milk depending on calcium content were investigated. It was found that during decalcification of skimmed milk, appearance of vitreous appearance is observed at stable consistency, taste and smell. This is a consequence of destruction of the caseinate-calcium-phosphate complex with a simultaneous decomposition of the casein micelles to sub-micelles. It was established that the change in the chemical composition of milk including mineral composition of the ash residue is interrelated with the amount of removed calcium. There was a decrease in the weight fraction of dry matter including non-essential decrease in proteins and an essential decrease in lactose as well as the values of active acidity and optical density.

2. Qualitative properties of protein clots and whey obtained at various calcium contents in raw materials were established. It was shown that reduction of calcium content in milk results in a lower density of the fermented clot and its moisture-discharge ability. At the same time, an increase in the weight fraction of dissolved protein in the whey is

observed which is explained by the transition of casein submicelles to a soluble state.

3. Effect of calcium content in skimmed milk on organoleptic, physical, physical-chemical and technological properties of fermented-milk cheese was investigated. The rational degree of decalcification of skimmed milk (20–25 %) has been established for obtaining fermented-milk cheese with new quality indicators. It was proved that decalcification of milk at the indicated parameters makes it possible to obtain fermented-milk cheese characterized by a spreadable consistency, absence of crumbs and whey separation, with high values of MRA (52.2±1.0 %) and dispersion. Expansion of technological purposiveness of the new product for restaurants was predicted.

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