1. Introduction

Modern technology of dairy products manufacturing is characterized by the improvement of separate technological stages with the emphasis on retaining quality, as well as quantity.

In recent years, there has been an increase in prices for basic raw materials and ingredients for the production of...
semi-finished products based on milk-protein. It is difficult to store them at low temperatures without losing the ingredients of animal origin for semi-finished products, defrosting of which is accompanied by a decrease in weight indicators. Thus, the industrial method of freezing in large volumes is considered to be most effective [1], since it provides instant, shock freezing that contributes to retaining nutritious substances of milk-protein concentrates; along with this, the process is accompanied by the loss of the overall weight [2].

The structure of market for frozen food in Ukraine has its own peculiarities. Segments of vegetables and berries prevail in the European countries [3, 4], while the products that are characteristic of national culinary tradition prevail in Ukraine. Pancakes, casseroles, ready meals (cheese-cakes, benderiki), in addition to the segment of dumplings, are present in the market of semi-finished products [5]. The classical raw material, which is included into the formulations of semi-finished products based on milk-protein, is sour-milk cottage cheese, wheat flour, manna groats, sugar, blend, fillers, etc.

One of the main problems for manufacturers of semi-finished products is not only to provide milk-protein raw materials of appropriate quality, but also the possibilities of its conservation. Given the tendency to reduce production of cottage cheese, and to increase its cost, the improvement of the methods for long-term storage of raw materials is a relevant task. It is a common practice to freeze milk-protein raw materials for further use in the technology of melted cheeses and half-finished products – the products that are exposed to repeated heat treatment [6].

Introduction of technologies of various semi-finished products and dessert products based on cottage cheese attest to the prospects of the further research in this field. The absence of technological solutions regarding the improvement of the storage of milk protein concentrates by freezing and intensification of the production process makes the search in this direction relevant.

In addition to the classic milk-protein basis – sour milk cottage cheese, it is possible to use the albumin mass for half-finished products. The degree of extraction of whey proteins is about 40 % [7]. An incomplete separation of proteins is due to the protective effect of electrolytes that exist in whey and the predominance of the charge of protein particles as a stability factor [8].

Improvement of the methods for extracting proteins from whey and the use of products in various technologies as the basis or the fortifier is relevant. According to the classical technology, the albumin mass is obtained by the thermal-acid coagulation, which involves whey processing at the temperature of above (95±1) °C and nearly (90±2) min, which is energy-intensive.

Based on the analysis of information about extending the terms of storage of raw materials and dairy products under production conditions, it was proved that freezing is most effective [9–11]. This applies to raw materials for semi-finished products – sour milk cottage cheese (SMC) and albumin mass (AM). Reserving by freezing is relevant from the point of view of leveling the effect of seasonal provision with raw materials.

Traditional defrosting techniques do not ensure maintaining the quantitative and qualitative indicators of sour milk cottage cheese [12]. Under any conditions of freezing milk-protein concentrates, there is a range of irreversible changes associated with protein coagulation. The three-dimensional structure of casein undergoes the ruinous impact. This leads to a decrease in the strength of curd and the ability to retain free moisture and results into the loss of weight at defrosting [13, 14].

Additional research and technological solutions in this direction are relevant.

The features of the production of semi-finished products make it possible to produce protein-plant mixtures from the traditional ingredients, such as sour milk cottage cheese and wheat processing products, included in formulations, before the lengthy storage at negative temperatures as early as at the cooking stage.

Given the moisture binding properties of manna and extruded groats [15], the inclusion in the formulation of milk-plant mixes for freezing and development of the appropriate technology will contribute to the conservation of raw materials for semi-finished products.

The use of albumin mass, obtained from whey, which is characterized by high biological value, will contribute to saving milk protein [16].

2. Literature review and problem statement

The process of freezing is accompanied by the formation of crystals and the mechanical damage of the structure of milk-protein concentrates. The formation is crumpled, punctured, and parts of the system are separated. This helps catalysis of hydrolytic reactions and influences the character of the flow of enzymatic processes in the product. The smaller the dimensions of ice crystals, the weaker the freezing influence on qualitative indicators of the defrosted protein concentrate, so a directional impact on the crystal formation process is important [17]. In general, the problem is the loss of weight of milk-protein concentrate in the freezing-defrosting cycle due to effluence of free moisture.

The process of lowering the product temperature that is significantly below the cryoscopic temperature is called freezing. During freezing, almost all the water contained in milk-protein concentrates, including sour milk cottage cheese, is crystallized. This is achieved if the temperature in the center of the product is minus 6 °C and lower [18]. There is a whole range of changes in the are of freezing. Firstly, it is a phase transition of water into ice. This change has a more complex character in the food system than at freezing of fresh water, including many other changes associated with this phase transition [19, 20].

The proportion of water as part of albumin mass is 65...80 % [21]. This significantly affects the state of proteins and, accordingly, the structure of AM after defrosting. The ratio between free and bound moisture, as well as the degree of its structuring are decisive factors in the formation of rheological parameters of food systems. In this case, the moisture structure, rather than total moisture, has the determining influence on the organoleptic, physical and chemical properties of milk-protein products [22]. The negative effect is the weight loss at defrosting of the above-mentioned products.

It is advisable to implement technological measures for retaining moisture by plant ingredients with moisture binding properties at the stage of preparation for freezing milk-protein concentrates (cottage cheese and/or albumin mass).
According to the literature data [23, 24], the effectiveness of using plant ingredients that underwent moisture and thermal treatment have increased structure forming properties and were already used in formulations of food products. The grain processing products (GPP), such as malt and extrudates were used as moisture-binding ingredients in the production of cottage cheese products [25, 26]. The method of extrusion treatment has a number of advantages: the absence of any chemical preparations, an increase in digestibility of its protein-carbohydrate component, and obtaining a product of sustainable quality and low cost. As a result of extrusion, manna groats loses free and partially bound moisture, acquiring an increased ability to absorb moisture. In addition, extruded manna groats is a source of valuable protein, readily available carbohydrates, microelements and vitamins. It is known that the amount of starch, dextrines and amylose in MG is, respectively, 55.3; 2.83; 0.23 % of dry substance; for EMG, these values make up 44.2; 20.02; 1.43 % [27, 28]. The difference can be explained by the fact that the destruction of large molecules of polysaccharides occurs during extrusion, which substantially changes rheological properties of a product. The obtained results of moisture retaining ability are higher than those of the above specified raw materials at the level from 68 to 7 % [25]. The problem is the lack of sufficient information [15] on the impact of the above-mentioned ingredients on the state of moisture in milk-protein concentrates during freezing.

During extrusive treatment of starch raw materials, specifically, manna groats, the total content of starch decreases due to spinning of amylose and amylpectin molecules, along with this, number of oligosaccharides and dextrines increases. This causes an increase in solubility and the degree of swelling of extrudates compared to the raw material, which did not undergo moisture and thermal treatment [29, 30].

According to literature data, [31] manna groats (MG) and extruded manna groats (EMG) that are supposed to be introduced to the mixture before freezing have the following chemical composition, %: weight fraction of moisture – 14; proteins – 10.3; lipids – 1.0; fiber – 0.2. The content of starch and low molecular carbohydrates in MG is respectively 54.3 % and 0 %. The corresponding values for EMG are 44.1 % and 1.1 %. The content of ash is 0.5 % for MG and 3.3 % for EMG.

Based on the scientific literature [32, 33], we stated the criteria for the selection of grain processing products for using in frozen protein-milk mixtures based of cottage cheese and/or albumin mass for further use in semi-finished products:
- appropriateness of an ingredient by the content of basic substances, quality indicators, solubility, tolerance, thermal stability, and cost;
- the lack of adverse effects on the chemical composition of milk-protein base, stability at repeated thermal treatment;
- compatibility of the composition and properties of food systems (principle of action, interaction with other components, a positive role of an ingredient in a food system);
- the possibility of evaluation of the effectiveness of its introduction by the existing indicators for milk-protein products;
- the possibility of combining by the classic formulations with maintaining organoleptic parameters of the finished product;
- competitive economic evaluation of the technological solution.

The percentage of introduction of a plant ingredient of 6...7 % is related to a minimum number of similar formulation components, specifically, wheat flour, in traditional semi-finished products based on sour milk cottage cheese [34, 35].

It is possible to predict the efficiency of the use of albumin mass as raw material in mixtures with cottage cheese for freezing in order to increase raw material resources. The quality of protein mixtures is significantly influenced by dimensions, shape and distribution of ice crystals that are formed in frozen AM [19]. The last statement requires additional research.

Albumin mass together with sour milk cottage cheese is recommended to be used as the milk-protein basis for food products that are exposed to repeated heat treatment and long-term storage.

According to the classical technology, disaggregation of protein associates occurs at the beginning of heating as a result of an increase in the velocity of particles, and agglomeration of protein globules, caused by their denaturation, occurs starting with 50...65 °C. Such proteins, losing stability at 75...80 °C – visible coagulation – form flakes. Optimum temperature of exposure is 90...95 °C [8, 36–38]. Optimal reaction of the environment is pH 4.4...4.6, which corresponds to titrated acidity of 30...35 °T, as well as to the isoelectric point of thermolabile whey proteins (lactalbumin faction) [39, 40].

Incomplete separation of proteins is caused by the protective effect of electrolytes that are present in whey and the predominance of the charge of protein particles as the factor of stability. To enhance thermal coagulation, reagents-coagulants – whey with acidity (150±5) °T – are introduced to cottage cheese whey. The process is lengthy, accompanied by losses of whey proteins [41]. The solution of these problems requires additional research.

There is a production practice of using “Collagen pro 4402” in the amount of 0.4 % to increase the yield of sour milk cottage cheese [42]. Positive results of this technological solution contribute to the expansion of the application of a collagen-containing ingredient and facilitate carrying out additional research into coagulation of whey protein in order to raise the yield of albumin mass under the classical conditions.

The improvement of the methods of extracting proteins from native or concentrated whey and their use in technologies of semi-finished products as the basis or a fortifier is relevant [41].

There is not enough information about the impact of negative temperatures on the moisture state in the albumin mass during prolonged storage and after defrosting.

The intensification of the process of thermo-acid deposition of whey proteins and the results of research into the influence of technological ingredients on the indicators of frozen milk-protein mixtures can be used for effective functioning in production systems.

The actual problem is the lack of a comprehensive approach to solving the tasks set in the framework of the review. That is why there are some grounds to consider that the lack of certainty of the influence of grain processing products on qualitative and quantitative indicators of frozen milk-protein mixtures (cottage cheese and albumin mass) determine the need for research in this direction.
3. The aim and objectives of the study

The aim of this work was to study the impact of grain processing products on the stability of qualitative and quantitative indicators of milk-protein mixtures after defrosting.

To achieve this aim, the following tasks were set:

- to explore the ways to intensify the deposition of albumin mass at thermo-acid coagulation from the liquid whey protein concentrate obtained by the method of ultrafiltration;
- to determine the cryoscopic temperatures of albumin mass and mixtures based on sour milk cottage cheese with manna groats and extruded manna groats to establish the conditions of freezing;
- to determine quantitative indicators of protein-plant mixtures and albumin mass with “Collagen pro 4402” at defrosting.

4. Materials and research methods. Obtaining albumin mass with the collagen-containing ingredient and protein-plant mixtures

To intensify the process of thermal-acid deposition of AM, we used the modification of raw material through concentrating whey on the membrane setup and adding a collagen-containing ingredient.

The resulting CWPUF \[43\] met the following requirements: the weight fraction of dry substances was (16±2) %, the weight fraction of total protein was (10.5±3.3) %, titrated acidity was (125±5) °T. The study of the duration of thermo-acid coagulation of both native cottage cheese whey, and concentrated whey in the form of the above mentioned CWPUF was carried out in the following way. Albumin mass was extracted in a similar way every 5 minutes from 4 dm³ of whey and CWPUF after reaching the optimum pH of 4.4..4.6 and temperature of 90..95 °C.

A special feature was the additional introduction of the technological ingredient “Collagen pro 4402” to the whey at the initial stage of heat treatment. The collagen-containing ingredient was introduced in accordance with the recommendations of the manufacturer \[42\]. For the research, the range of application of “Collagen pro 4402” was expanded from 0.3 % to 0.5 %.

The protein concentrate and albumin mass in the research were used in the composition of protein-plant mixtures (PPM) to freeze and to determine the cryoscopic temperature by the method of thermal analysis \[44\]. As a control sample, we used sour milk cottage cheese and/or albumin mass with CWPUF with the weight fraction of dry substances of (16±2) %.

The study of the duration of proteins coagulation in:

\[
t 90…95 °C
\]

Yield of albumin mass, %

Fig. 1. Dynamics of accumulation of albumin mass in relation on duration of proteins coagulation in:

1 – whey; 2 – protein concentrate

For maximum separation of albumin mass form native whey, the effective coagulation time is (55±2) min, and with CWPUF, it is (40±2) min, respectively. It was proved that it is not advisable to perform subsequent temperature treatment because the product yield is not significant. Thus, the duration of the effective thermal treatment of sample 1 relative to sample 2 decreased by (15±2.3) min. In absolute values, the yield of albumin mass with CWPUF in (40±2) min amounted to 1,039.2 g, and for AM obtained from non-concentrated whey during the same time it amounted to 378.7 g, respectively.

The difference from the classical technology of obtaining albumin mass was introduction of “Collagen pro 4402” in the prepared state to the capacity for coagulation before the thermal treatment in the above-mentioned modes.

A change of the albumin yield depending on the amount of “Collagen pro 4402”, %, under the same conditions of the process is shown in Fig. 2. The obtained results of the AM yield were corrected by the amount of dry matter of the introduced collagen-containing ingredient.

5. Results of studying the influence of grain processing products on the indicators of frozen milk-protein mixtures

5.1. Intensification techniques for albumin mass deposition

At the first stage, we used the method of whey ultrafiltration to obtain CWPUF – raw material for AM.

Fig. 1 shows the dynamics of accumulation of albumin mass on the duration of the process of thermal-acid coagulation and the type of raw material – native whey or CWPUF with the weight fraction of dry substances of (16±2) %.

Fig. 2. Yield of albumin mass depending on the amount of “Collagen pro 4402”
According to the results (Fig. 2), introduction of 0.4% of “Collagen pro 4402” to whey increases the yield of albumin mass from the protein concentrate and whey on average by 25% under the same conditions of conducting thermo-acid coagulation.

At the next stage of work, the duration of coagulation of whey proteins with the collagen-containing ingredient was explored. Fig. 3 shows the dynamics of accumulation of albumin mass depending on the duration of thermal sedimentation under sustainable conditions.

According to the image (Fig. 5, a, b), cryoscopic temperature for the control sample (SMC) is minus 0.74°C; for the samples with the use of MG in the amount of 6% and 7% is minus 1.01°C and minus 1.14°C, respectively, and for samples from EMG in the same amount, it is minus 1.76°C and minus 1.82°C.

5.2. Studying the cryoscopic temperature of albumin mass and mixtures based on sour milk cottage cheese with manna groats and extruded manna groats

In order to reduce losses, it was proposed to introduce manna groats and extruded manna groats to sour milk cottage cheese, exploring the impact of the amount of introduced additives on the cryoscopic temperature of mixtures.

Fig. 4 shows graphically the dynamics of ice formation at freezing AM obtained from “Collagen pro 4402”.

Fig. 4 shows that the cryoscopic temperature of AM, obtained from “Collagen pro 4402”, is minus 0.6°C, and for the control sample (AM), it is minus 0.3°C. Analysis of the obtained results proves that the introduction of the collagen-containing ingredient during coagulation slightly increases the amount of water that does not turn into ice when freezing. The smallest amount of frozen moisture was established for the sample of AM obtained from “Collagen pro 4402”.

Fig. 5 shows graphically the dynamics of ice formation during freezing SMC with MG (a) and EMG (b) and of control sample (low fat sour milk cottage cheese).

Sour milk cottage cheese has the lowest value, and SMC with EMG in the amount of 7% has the lowest value, which confirms the theory of influence of carbohydrates of plant components on the moisture state.

Based on the values of cryoscopic temperature, we calculated the amount of frozen moisture in PPM, %, which is 88.75 for the control sample (SMC), while for the samples with adding manna groats in the amount of 6% and 7%, it is 86.61 and 85.54, respectively, and for EMG in the same quantities – 80.12 and 79.37.
5.3. Determining quantitative indicators of protein-plant mixtures and albumin mass from “Collagen pro 4402” at defrosting

The obtained results of studying the losses during defrosting PPM mass with different amount of MG and EMG are shown in Fig. 6.

![Fig. 6. Losses during defrosting PPM mass with different amount of MG and EMG](image)

Thus, when adding MG (in the amount from 5% to 8%), the losses of weight vary in the range of 7.8...6.9%. The smallest percentage of the loss is observed during the introduction of EMG to the protein basis – 7.31...4.47%. The control sample is low fat sour milk cottage cheese (weight fraction of moisture is 76.0%, titrated acidity is 206 T). The loss of its weight during defrosting was (9.0±0.4)%.

The losses of moisture during defrosting of the AM obtained according to the classical technology and the AM obtained from “Collagen pro 4402”, %, are shown in Fig. 7.

![Fig. 7. Losses of moisture during defrosting: 1 – AM (control), 2 – AM obtained from "Collagen pro 4402"](image)

The obvious release of moisture began after 2 hours of defrosting and finished after 3.5 hours, because the temperature in the middle of the sample amounted to 0 ºC. 15.2% of moisture were released from the sample of AM obtained from a collagen-containing ingredient, and 20.5% were released from the sample obtained according to the classical technology. This is probably related to the ability of “Collagen pro 4402” to bind partially free moisture in the AM, which promotes maintaining quantitative indicators and extending the storage terms.

6. Discussion of results of studying the influence of grain processing products on the indicators of frozen milk-protein mixtures

The presented material is continuation of the research aimed at reducing the influence of low temperatures on MPC (specifically, sour milk cottage cheese and albumin mass) by decreasing the amount of free moisture, which correlates with the value of frozen moisture.

The process of obtaining AM from CWPUF and with the use of collagen-containing ingredient was intensified. The time of thermo-acid coagulation decreased by (15±1) min compared with the use of native whey as raw materials under the same conditions of the process. An increase in the amount of collagen-containing ingredient up to the level of 0.45...to 0.5% is irrational because an increase in the yield of the mass only by 0.8...1.1 % within the same time of coagulation is observed. This phenomenon is explained by the fact that during boiling, a triple curl of collagen structure is destroyed and sub-units are partially hydrolyzed turning into gelatin. Extended chains of peptide – gelatins – attach a certain amount of water, including that from the water membrane of whey proteins with the formation of hydrated molecules. This causes dehydration of protein molecules, a decrease in the charge and sedimentation. Collagen prevents dispersing of coagulated albumin and wrapping of particles and contributes the sedimentation of flakes. It is recommended to use the resulting AM as milk-protein component of semi-finished products.

Cryoscopic temperatures of mixes based on sour milk cottage cheese with MG and EMG were determined. The change of these indicators compared with sour milk cottage cheese makes it possible to evaluate objectively the benefits of so-called cryptoprotectors. Extrudates ensure a decrease in losses during defrosting due to reducing the amount of frozen moisture. High molecular carbohydrates undergo aggregation during the process of freezing, and the process of retrogradation of the part of starch occurs, which leads to a decreased ability to bind water. The phenomenon can explain the loss of fluid during defrosting PPM. EMG retains its properties in the cycle of freezing-defrosting, due to the change in the starch component during moisture-thermal treatment at the temperature of above the temperature of gelatinization. The cryoprotective effect of carbohydrates is associated with the fact that hydroxyl group of carbohydrates cannot effectively embed H-bond into the crystal lattice of ice and prevent the buildup of large crystals. In insoluble polysaccharides that are a part of MG and EMG, inhibition of water mobility may be caused by long-acting forces of adsorption binding of water by surfaces of dietary fibers (fiber – 0.2%), which are the part of the above-mentioned ingredients [48].

The limitations of this study include the need to have a range of special equipment with the temperature control device, units of signal measurement and conversion.

The prospects of subsequent research are related to the selection of other plant components with similar properties to solve technological problems.

The practical outcome of scientific research is acceleration of the process of thermal-acid coagulation of proteins from CWPUF and with addition of “Collagen pro 4402”. This technological approach contributes to power saving and to solving the problems associated with the need for complete extraction of whey proteins.
Research into cryoscopic temperature of PPM proves the cryoprotective effect of carbohydrates of the extrudate of manna groats, which is important for retaining the native properties of the MPC during the storage at negative temperatures. The amount of the introduction of GPP is determined taking into account the assortment of semi-finished products. The research results are aimed at obtaining milk-protein concentrates and retaining the quantitative indicators in the freezing-defrosting cycle. Implementation of the technology is relevant for the production of milk-protein products.

7. Conclusions

1. It was established that the time of thermal-acid coagulation of whey proteins from CWPUF and from “Collagen pro 4402” in the optimum amount of 0.4 % at a temperature of 92...95 °C decreased by (15±1) min.

2. We determined the cryoscopic temperature, which is minus 1.01 °C and minus 1.14 °C for PPM with MG (6 % and 7 %), and minus 1.76 °C and minus 1.82 °C for PPM with EMG in above specified quantities, respectively. The highest cryoscopic temperature was recorded for sour milk cottage cheese (control sample), and the lowest – for PPM with EMG in the amount of 7 %, which proves the cryoprotective effect of carbohydrates of manna groats extrudate. An increase in the amount of EMG from 6 to 7 % reduces the amount of frozen water by 0.75 % at the temperature of minus 25 °C.

3. It was found by the weight method that with an increase in both the amount of MG, and EMG from 6 to 8 %, the losses of the weight of PPM after defrosting decrease. At adding MG in the above-mentioned amount, the loss of weight ranges from 7.8±0.2 to 6.9±0.1 %. The smallest losses of weight at the level of 4.47±0.1 % were recorded during adding 8 % of EMG to milk-protein concentrates at the stage of making mixtures before freezing.

References


