STRUCTURED SEMI-PRODUCT WITH THE USE OF GELATIN THE TECHNOLOGY OF CHEESE

The monograph

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The monograph includes concentrated and integrated scientific information concerning the use of nonfat cheese and sunflower seed kernel for producing structured products at the restaurant business enterprises. This information is presented in the form of text, technological calculations, figures, diagrams, tables and it is meant for lecturers, postgraduates, students who are engaged in scientific work.

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INTRODUCTION

When analyzing the state of the domestic cheese market, its poor quality and high cost caused mainly by lack of the base raw material – milk in its production should be marked out. Therefore, dairy plants produce cheese mainly in summer. In winter, its output is reduced sharply and production works due to the stocks made in summer and autumn.

In Ukraine the development of new composite cheese semi-products that compensate nutritional problems and have expressed curative and prophylactic properties is conducted. Production of cheese semi-products fortified with dietary supplements of plant origin allows expanding range of products, increasing competitiveness of functional semi-finished food products and their nutritional value. A significant contribution to the development of these technologies was made by N.P. Zaharova, E.G. Naydenova, A.O. Bovkun, S.S. Gulyaev-Zaitsev and other scientists, but their works were not related to the use of the concentrate of sunflower seed kernel.

Protein of sunflower seed kernel occupies an important place among the plant proteins used in food technologies. Ukraine has a large raw material base of this culture because our country occupies one of the first places in the world, particularly in the CIS, in terms of sunflower seeds production for obtaining oil. Thus, sunflower cake with a broad range of functional and technological properties is not used effectively and it is not widespread in scientific and experimental works.

Taking into consideration the above mentioned, the upcoming trend in creating new semi-finished food products with effective introduction of plant protein to the recipe is the development of scientifically grounded technology of cheese structured semi-product with the use of the concentrate of sunflower seed kernel. Thus, the use of the protein of sunflower seed kernel with cheese allows obtaining cheese structured semi-product with high nutritional and biological value, microbiologically and environmentally friendly and costeffective. In addition, the presented technology allows extending the range of cheese structured products in the consumer market of Ukraine.

The monograph contains materials that include specification and structural-functional properties of structure-forming agent, review of contemporary methods of the integrated use of milk raw material, particularly nonfat cheese with effective introduction of plant protein to the recipe and obtaining structured products on the base of this protein.

The first chapter presents analysis of the current state and prospects of structured products, the general specification of dairy proteins of cheese; consideration of their physical-chemical, functional-technological and structural-mechanical properties as well as substantiation of reserving cheese by freezing; prospects of the use of concentrate of sunflower seed kernel and gelatin in structured products composition; analysis of the chemical composition

of sunflower seed kernel; functional properties of gelatin.

The second chapter contains materials focused on substantiation of technological parameters of the structured products on the base of nonfat cheese thawed; substantiation of the recipe ingredients content, the choice of the structure-forming agent, fat ingredient; investigation of the structuralmechanical properties of the model system of cheese structured semi-product; investigation of the mechanism of complex formation of the model system ingredients.

The third chapter is devoted to the development of the recipe composition and technology of cheese structured semi-product on the base of nonfat cheese thawed with the use of sunflower seed kernel, with addition of refined deodorized oil and food vegetable oil as fat ingredient and gelatin as a structure-forming agent. Nutritional and biological value of cheese structured semi-product, safety indices, terms and conditions of storage, quality indices and recommendations on the use of cheese structured semi-product as a part of culinary products.

CHAPTER 1

MODERN TRENDS IN DEVELOPING TECHNOLOGY OF STRUCTURED PRODUCTS BASED ON NONFAT CHEESE AND PERSPECTIVES OF THE USE OF SUNFLOWER SEED KERNEL

1.1. Analysis of the current state and perspectives of developing the technology of structured products based on cheese

Nutrition system of a contemporary human is closely related to the socio-economic condition of the state. High level of poverty of the population of Ukraine, low subsistence level, deterioration of food products quality under conditions of economic crisis as well as the increase in consumption of food products of in industrial production result in a significant deterioration of nutritive status and state of health of population, especially in children and young people [24, 28, 29, 85, 108, 236, 238].

The processes of globalization in Ukraine taking place in the sphere of providing population with food products when under conditions of global economic crisis most manufacturers seek to reduce the cost of their products due to the use of dietary additives stipulate a real threat of deterioration in the quality of food products.

The market of milk and dairy products is one of the leading in the structure of the food industry of Ukraine. The main factors that hinder development of the domestic dairy products market are: reducing the number of cows, poor quality of raw milk, outdated technology, non-conformance of national standards and requirements concerning milk quality to European ones [144]. According to statistics [10, 31, 78, 86, 118, 203, 204] since 1990 the volume of milk production in Ukraine has decreased by 54.3%, first of all due to the agricultural enterprises and small farms and households had been the actual monopolists of producing milk as raw material during 2000-2010. This trend causes problems for dairy industry, first of all due to technological failure of private farms of the population to provide high quality of raw milk [85, 103-106].

These negative trends in the development of dairy farming have led to a reduction in the supply of raw materials for industrial processing practically fourfold during the period of 1990-2010 [103-106, 144, 153].

However, throughout the whole period there was a tendency of reducing annual consumption of milk and milk products by population of Ukraine in total – by 46.6% or from 373 kg (in 1990) to 206 kg (in 2010) per person corresponding to 54.3% of the rational consumption norm [153].

Cheese and products on its base are very popular in our country. When it comes to diets and most useful products then you can not do without cheese [4, 72, 103-105].

The high content of valuable milk protein, calcium and phosphorus, different amounts of fat make this product essential for all who are concerned about healthy diet [24, 28-30, 32, 108, 223, 224].

Curd in one form or another cottage cheese is included in the diet of about 80% of the population of Ukraine. Standard 100gr pack of cheese satisfies 70% of the average daily requirement for protein. Protein contained in cheese has an adequate acid composition and it is easily digested. Fat included in cheese composition is very important for a balanced diet of people. It replenishes energy costs and performs structural-plastic and protective reactions in the body. Butterfat has the most difficult chemical composition of all fats of animal and vegetable origin. However, its fat and acid composition is not perfect. Increase of biological value of cheese can be achieved by modifying fat and acid composition due to the use of vegetable oils. Moreover, simultaneous use of protein raw material of milk and vegetable origin under conditions of high cost and shortage of quality raw milk as well as growing competition from the imported products allows ensuring its competitiveness, expanding range of products and reducing costs [52, 203].

Under modern conditions of production, dairy enterprises pay great attention to the expansion of the range of products with low production cost and high nutritional value. However, a growing interest from producers and consumers to the products based on cheese is observed. So, in this sense, a special interest is attracted by the possibility of using cheese as a protein base due to its functional properties in structured products technology of [106, 107, 110-113, 146].

Cheese as a source component for obtaining structured products can be considered as a concentrated suspension of casein particles in a solution of proteins, salts and other hydrophilic substances [18, 66, 67, 72].

It is known from the literature sources [3, 4, 7, 16, 18, 22, 34, 35, 47, 48, 70, 71, 74, 80, 147, 239] that production technology of traditional structured products based on cheese, as a rule, does not involve the use of protein-lipid raw materials of vegetable origin. Structure formation and maintenance of high nutritional value is achieved by the use of fat-containing recipe components, the composition of which include emulsified fat that is "natural" emulsions - milk, cream, sour cream, butterfat, melange.

However, in recent years there has been a tendency to create combined structured products with desired composition and properties. Such products must comply not only with modern medical and biological requirements, but also the traditions and habits prevailing among the population [119]. Products based on nonfat cheese with addition of ingredients of vegetable origin became widely-used among combined products. At present time a lot of technologies of products that involve the use of soya, pectin, barley malt extract, cereals are developed [130, 132, 134, 147, 190, 192].

Decrease in density of protein cheese, butterfat melting that leads to deformation of the product occurs while conducting heat treatment of structured products based on cheese with high fat content. Raw material that serves as a

structure-forming agent (eggs, flour, semolina) due to albumin denaturation, formation of gluten network of flour protein or absorption of water by gelatinized starch is used to prevent this [40, 41]. Other raw materials that are added (some dairy products, sugar) together with structure-forming agents contribute to the regulation of nutritional and biological value of the ready-toeat meals. Introduction of different types of fillers (vegetable, fruit, cereal, etc.) allows increasing such important nutrients as dietary fiber, minerals and vitamins while reducing a certain amount of protein and fat.

Introduction of vegetable components in structured products based on cheese allows not only using efficiently milk protein raw material but also fortifying processed food products with carbohydrates, vitamins, valuable proteins and minerals [80, 110-113, 142, 173, 175, 177-181]. Vegetable and animal proteins complementing each other create rather active biologically amino acid complexes that provide interstitial synthesis. Thus, the total amino acid formula becomes more valuable biologically. That is why considerable attention of specialized research institutions and manufacturers has been recently paid to the structured products based on cheese with the use of raw material of vegetable origin. [44].

In comparison with butterfat vegetable oils have a number of advantages conditioned by the absence of cholesterol, the presence of vitamins, essential polyunsaturated fatty acids which contribute to cholesterol excretion.

Upon the analysis of the currently in use developments it can be stated that food additives based on vegetable raw material that allow obtaining finished products with increased nutritional and biological value, various recipe composition by means of which it is possible to extend range of products and reduce production cost become widely-used in production of structured products based on cheese.

1.2. The characteristic of chemical composition, functional and technological properties of cheese protein

Among dairy products which are in increasing demand the leading place is occupied by cheese which is considered to be an essential product for adults and children, for elderly people and patients [217, 221, 225, 230].

Cheese is a product that has high nutritional and biological value due to quite large content of protein and minerals (calcium, phosphorus, iron, magnesium, etc.). It is considered to be the product of all-purpose use and it distinguished by its high digestibility according to its chemical composition [18, 29] and that is why it is essential in a daily diet of each person [28-30, 32, 41, 109, 127, 202, 219, 221].

Cheese starter cultures of direct introduction (DVS-cultures) and CHY-MAX milk-coagulating enzyme are effectively used in current technologies to increase cheese yield by 8%. Composition of this enzyme is characterized by a 100% content of chymosin as an active enzyme that has a direct action to split casein that conditions obtaining a quality bunch with release of transparent greenish whey without presence of protein [18, 142, 202].

According to the way of coagulation cheese is classified into acid and acid-rennet. Typically, acid cheese is made from skimmed milk.

During cheese production coagulation of proteins (with destruction of colloidal system of milk) occurs with decreasing negative charge of casein and transferring it into isoelectric state by adding, separately or in combination, acids (acid coagulation), rennet (rennet coagulation), by adding calcium chloride (calcium coagulation) [170, 217].

Coagulation phase details of which still are not adequately explored is a biochemical reaction that leads to aggregation of micelles. At the same time it is possible to consider hydrophobic links between residues of para-χ-casein, salt junctions (calcium and calcium phosphate) between α_{s1} -, α_{s2} - and β-casein, probably disulfide junctions between para-χ-casein and others. Micellar para-χcasein has a pronounced hydrophobic character that is as a result of a bimolecular reaction generally hydrophilic source micelle gains hydrophobic areas that results in the appearance of phase separation surface and respectively increase in free (excess) interfacial energy that according to Gibbs-Helmholtz principle tends to spontaneous reduction in disperse systems [18, 66, 67, 72, 198, 201]. This process leads to decrease in entropy of the system as a result of increasing the proportion of ordered elements in the structure of surrounding water (hydrophobic interactions between molecules of para-χ-casein and water molecules are accompanied by the increase in entropy and transition of the system to a more favorable energy state). Also combining micelles into a single, compact structure that provides the least contact of hydrophobic areas with water is energetically favorable for the system. In turn, contacts between the same hydrophobic areas also lead to decreasing free energy of the system [66, 72, 217].

It should be noted that chemical composition of cheese varies depending on its fat content (Table 1.1) [9, 10, 11, 64, 72, 199]. Nonfat cheese has protein content of 4-6% more than fat one. At that the amount of fat in nonfat cheese does not exceed 2%, and in fat cheese - in the range of 2 to 18%.

According to free amino acids content (Table 1.2) cheese obtained by continuous method based on coagulation of proteins in the stream is slightly inferior to cheese obtained by periodic method but has better water-retaining property [72, 92].

Table 1.1

Chemical composition of cheese

Obviously, the differences in the content of free amino acids in cheese of investigated kinds is conditioned by the fact that in the production of cheese by periodic manner the starter acts in better conditions and for a longer time than in the production of cheese in a coagulator. However, the content of free amino acids in cheese produced by continuous method while proteins coagulation in the stream can be improved by selecting the appropriate amount of bacterial srarter [72].

Table 1.2

Amino acid composition of cheese proteins

Data of Table. 1.3 also show a high biological value of cheese which is conditioned by the content of all essential amino acids (lysine, tryptophan, threonine, valine, methionine, isoleucine, leucine, phenylalanine).

Describing chemical composition of cheese its high calorie value should be taken into account: 100 g of fat cheese is $233...253$ calories, 100 grams of nonfat cheese is 75...86 calories, 100 grams of beef is about 135 calories, 100 grams of fish is about 46 kcal [199, 224].

The content of calcium and phosphorus salts in cheese is in the ratio the most favorable for digesting by a human body $(1,0:1,5...1,0:2,0)$.

Cheese obtained by continuous method contains \sim 124.2 mg% Ca on average, by periodic method \sim 117.5 mg% and phosphorus \sim 90.3 and \sim 77.0 mg% respectively.

Cheese obtained on the base of milk protein coagulation by continuous method in a stream has water-retaining ability by 6...8% more than that one obtained by periodic method presumably as a result of partial denaturation of whey proteins during pasteurization of milk that is by $8...10^{\circ}$ C higher than during the production of periodic method (Table 1.3).

Table 1.3

Dependence of water-retaining ability of cheese protein on pasteurization temperature

Interaction of denatured β-lactoglobulin with casein micelles occurs during high-temperature treatment of milk. Whey proteins has more hydrophilic property compared to casein that results in increasing its water-retaining ability and thermal stability. Hydrophilic properties of casein in turn affect the ability of acid and acid-rennet cheese hold and release moisture. Change of hydrophilic properties of casein should be considered when choosing pasteurization standard in the process of manufacturing fermented milk products including cheese [88, 202, 218].

Cheese produced by acid-rennet method has homogeneous, rather plastic consistency [72] and that one produced by acid method is characterized by heterogeneous, lumpy consistency. That as suggested by the author [66, 67] is related to the fact that the main valence bonds do not break during acid fermentation of milk. Therefore, tertiary and secondary protein structures do not swivel enough that limits surface activity and formation of spatial protein structures.

Cheese has thixotropic structure of coagulation type (able to restore after mechanical destruction). Between protein particles there are liquid layers that reduce the structure strength but at the same time they provide its plastisity and elasticity. Properly selected strain composition of starter cultures allows regulating actual acidity of the cheese and keep pH value in the range of 4.5...4.8 that is important for obtaining dense cheese and forming the product's taste [72, 218].

Casein relates to phosphoproteins [202] that is it contains residues of phosphoric acid (organic phosphorus) attached to serine amino acid by monoether bond (O-P), α_s -casein has eight residues of phosphoric acid in the polypeptide chain, β-casein - four and χ-casein - one.

Polar groups located on the surface and inside casein micelles (NH₂, COOH, OH, etc.) are associated with ionic and molecular adsorption that plays an important role in the hydration of protein molecules. In many cases stability of protein colloid depends on the ionic adsorption. Ion adsorption is provided by free polar groups of protein – carboxyl, amine, hydroxyl by forming polar centers on a protein molecule they dissociate in solutions, acquire a charge around which water dipoles are oriented that are located in layers near the centers of a protein molecule and forming a hydration shell. The first layer is oriented motionless water molecules firmly linked to protein – bound, hydration moisture of molecular adsorption. The rest of the layers are moisture of multimolecular adsorption that under certain conditions does not differ from the free one. Linked polar groups of protein - peptide, main polypeptide chains, hydroxyl, sulfhydryl provide molecular adsorption as a result of charge ignition due to offset of the common pair of electrons to one of the atoms. The onset of the difference of potentials causes the orientation of water dipoles [138-141].

Polar groups of protein bind large amounts of water: \sim 1.9 g per 1 g of protein. The ability of casein to bind water is characteristic of its hydrophilic properties. The latter depend on the structure, charge quantity of the protein molecule, pH environment, degree of dispersity of protein substances, salts concentration and other factors. They are of great practical importance in the technology of structured products [45, 72, 138, 217].

Casein in the form of micelles of a nearly spherical shape is present in fresh milk. The average diameter of its particles is 70...100 nm (ranging from 40 to 300 nm) and molecular weight - about 108. In turn, casein micelles are composed of subunits (submicelle) of diameter of 8...15 nm and molecular weight of 250,000...300,000 Da [66, 67].

The changes that occur with milk proteins during milk treatment and processing are of great interest for scientific research. Milk contains on an average 2,9...4,0% of proteins, including 2,3...2,9% of casein and 0,5...0,8% of whey proteins. The main protein of milk is casein. It amounts $78...85\%$ of the total milk proteins, 15...22% of whey proteins [45, 66, 67].

Interaction of the denatured β-lactoglobulin with casein micelles occurs during high-temperature treatment of milk. Whey proteins are more hydrophilic compared to casein that results in increasing its water-retaining ability and thermal stability. In turn, hydrophilic properties of casein affect the ability of acid and acid-rennet cheese hold and release moisture. The change in hydrophilic properties of casein is taken into account when choosing a mode of pasteurization in the production of cheese [72, 201, 241].

Thermal stability, ability to coagulate under the influence of several factors: heat, hydration, proteolytic cleavage, etc. play an important welldefined role in the processes of producing dairy products including cheese [45, 80, 104, 157, 161].

Casein can be classified into the following fractions: : α_{s1} , α_{s2} - β-, γ casein, the rest of its factions are derived from one of the above mentioned phosphopeptides [201, 217, 226, 228]. α_{s1} -, α_{s2} - β-, γ-casein fractions are wellinvestigated. They can be isolated in quite a pure form, their amino acid composition and partially structure are known. Casein in milk is present in the form of a colloid solution of gel (particles of fine substance are uniformly distributed in a liquid medium) in the form caseincalciumphosphate complex which is formed by a combination of calcium caseinate and calcium colloid phosphate [45, 67, 72]. When increasing acidity or introducing rennet milk protein coagulates forming cheese-gel. With aging cheese (gel) compresses and it releases water (whey) with substances dissolved in it (syneresis occurs) [221].

Nonfat cheese, which contains milk protein (casein) as the main constituent, is presented in the form caseincalciumphosphate complex (CCPC) [66] with pronounced hydrophobic bonds mainly due to the «calcium bridges» of pair-χ-casein (Fig. 1.1). Hydrophobic interactions of these proteins lead to the formation of clusters of protein particles (micelles) combined into a single structure that provides the largest contact of proteins with water [45, 66, 67].

A few models of casein micelles are suggested [45, 66, 67, 72, 201, 217], among which, in our opinion, the most reasonable model is proposed by G. N. Krus [67]. According to her theory, casein micelle consists mainly of three types submicelles (Figure 1.2) (A) - α_s -casein + γ -casein, (B) - α_s -casein + β-casein and (C) - β-casein + χ-casein.

Formation of submicelles (A) occurs mainly due to the forces of electrostatic and hydrophobic interactions. Formation of submicelles (B) occurs as the result of hydrophobic and electrostatic interactions as well as due to calcium ions or calcium colloidal phosphate (CCP). Submicelles (B) interact with each other with the help of using CCP and form a complex that is the main part of a micelle core. During its formation submicelles (C) and some of submicelles (A) interact with submicelles (B) [66].

When χ-casein content exceeds critical concentration of micelle formation, than a micelle is completely formed. In this case χ -casein in submicelles (A) manifests itself as a typical surfactant. Submicelles (A) trying to selfassocciate cover micelle core and deposit on its surface. Thus, bonds between submicelles (A) and (B) are formed due to CCP and micelles growth is terminated. Submicelles (A) are located on the surface of the micelle in such a way that the N-end of χ-casein is focused inward the micelle, and the C-end of χ-casein is located on the surface. Thus most part of the micelle surface is covered by the C-end of γ -casein that has filamentary, branched structure due to

carbohydrates and form so-called "hair coating" on the micelle surface [96]. Micelle is constructed so that the hydrophobic sites of casein molecules are hidden inside and hydrophilic groups of χ-casein which form hydration shells with thickness of a mono- or bimolecular layer are located outside. Besides, casein micelles due to basic and acidic groups of atoms have different polarity so the forces of attraction and repulsion act simultaneously between micelles. Minimum repulsive forces are observed in the isoelectric point of casein [45, 67, 109, 201].

Water-binding and water-retaining ability and consistency of cheese depend on the hydrophilic properties of casein and its cleavage products. Thus, the hydrophilic properties of casein do not only determine stability of the protein particles in milk during its processing, but also affect the course of some technological processes. Casein like all proteins contains both amine $-$ NH₂ and carboxyl – COOH groups that are present in the solution in the form of NH_3^+ and COO⁻. Thus, casein has properties of amphoteric electrolyte (ampholyte, zwitterion). The number of free carboxyl groups in casein are larger than in amine, so it has an acid reaction [45, 49, 66, 67, 217].

The speed and stability of binding water depends mainly on the condition, properties and concentration of protein substances. Moistureretaining capacity of proteins that are investigated in the works [7, 45, 48, 50, 85] are significantly affected by their natural properties: the presence of charged polar and free polypeptide groups; spatial structure of protein; the value of the specific surface of protein particles. Hydration conditions also have significant impact: value of pH environment; degree of denaturation changes; concentration and properties of electrolytes in the systems of melting salts.

The ability of casein to bind water is of great importance in terms of technology. It contributes to its thermal stability that allows heating milk not only to the pasteurization temperature of 72...95°C, but also to the temperature of sterilization within 150° C without causing its denaturation. During hightemperature processing of milk, its hydrophilic properties are enhanced due to the interaction of casein with whey proteins. Intensity of this interaction and temperature affect directly the structural and mechanical properties as well as moisture-binding and moisture-retaining capacity of the finished product [201, 217].

Formation of moisture-binding and moisture-retaining capacity as a result of the interaction of the "protein-water" system is one of the most important functions of milk protein that allows using it in production of the structured product on the base of cheese.

The study of the chemical composition, physical-chemical parameters, biological value, nutritional properties and behavior of milk proteins as a result of influence of various factors on them is the theoretical basis for improving the existing and developing new ways of separating proteins and products based on them [45, 92].

Proceeding from the fact that the colloidal system of "protein-water" which is CCPC is in equilibrium, and taking into consideration the tendency to denaturation of cheese protein during heating, the authors [67, 72, 139, 217] proved that to increase hydrophilicity and to provide aggregative equilibrium of milk protein during heating it is necessary to raise its negative charge. Thus, cheese can be used as a protein basis and milk casein in the form of CCPC as a stabilizer of heterogeneous system in recipes of structured products.

1.3. Substantiation of cheese reserve by freezing

With a total annual production volume of more than 20 thousand tons in Ukraine its output during a year is non-uniform [20, 78, 160]. To adjust consumption part of the cheese is frozen in summer and it is stored in this form for 3-12 months and then it is realized during the period of small supply of milk for processing thawing it beforehand. Thus, the quality of cheese depends on conditions in which freezing, storing and thawing are conducted. Nowadays, this process is still poorly investigated.

The expressed seasonality in production of cheese indicates clearly the need for long-term storage. Under conditions of the expansion of production and establishment of the milk and dairy products market, freezing preservation allows preserving the quality of cheese during off-season, creating a sufficient amount of reserves for production and trade.

At present stage of development freezing is considered worldwide to be the most effective and promising way of extending shelf life. Low temperature slows down the course of microbiological and biochemical processes that may lead to a change in product quality indicators [89, 114].

Investigations on low-temperature storage of dairy products provided the basis for research and improvement of cheese storage technology [9, 27, 38, 59, 68, 69, 89, 154, 191]. Its organoleptic properties during the prolonged storage could deteriorate as a result of enzyme activity, water motion and the quality of packaging material. Low temperatures of refrigerated processing allow preserving cheese quality for 6-8 months at a temperature of -8° C. Short increase in shelf life of cheese for 7...14 days can be guaranteed by other means such as the use of structure stabilizers the and appropriate heat treatment [159].

Solving the problem of manufacturing cheese structured semi-product it is necessary to organize reservation of the main recipe ingredient - cheese and throughout the year to supply high-quality, sound product to market.

However, the problems with freezing, storage and thawing cannot be considered completely resolved despite the large number of opinions, recommendations and often contradictions of all sources [2, 15, 16, 27, 38, 54, 59, 68].

Leaving aside the controversy, in our opinion, it is useful to consider the process of freezing and storing cheese from two perspectives. Comparing the results of contemporary research on storing cheese it can be stated that some

of the authors investigated freezing, some of them investigated storage at low temperatures, some - thawing, but there are no data which would present the results of technological process of low-temperature reserving cheese. It should be noted that the stages of this process are closely interrelated and their absence will inevitably have an impact on the results of the former - thawing [55, 89, 126].

The second position is that before 2007 the enterprises of Ukraine worked according to the regulatory documentation of USSR. At that nonfat cheese (fat content - $0.4 \dots 0.6\%$) and fat cheese (fat content - 9% and 18%) was produced.

Since 2007, regulatory standards of Ukraine for cheese have been approved (DSTU 4554-2007 order №76 of 04.04.07) [165], where its classification is presented: nonfat cheese with weight fraction of fat less than 2% and this index is not standardized; cheese with weight fraction of fat over 2% to 18%. Physical and chemical properties of this cheese are presented in Table. 1.4.

Numerous investigations conducted in our country and in many other countries were devoted to the peculiarities of storing different kinds of cheese and cheese products in a frozen form [2, 14-16, 54, 55, 114, 126, 154, 191, 231].

Table 1.4

Characteristics of physical and chemical indices of cheese

According to the investigations of N.N. Filchakova and others, the perspective way of cheese refrigerated processing is its fast freezing in an air stream, apportioned in blocks of 0,20-6,0 kg and packed in polymer film. Another way is known. Cheese in the form of block was frozen on the contact surface of fast-freezing apparatus in the temperature range from -10 to -15° C [13, 55, 89]. High quality is guaranteed during 8-12 months at a temperature in the refrigeration chamber of -18° C. However, thawing in the air environment at a temperature of 20-35° C resulted in loss of weight of 18% and higher [13, 89].

To increase the shelf life of cottage cheese researchers [2, 89]

suggested conduct cheese granules freezing by air treatment at a temperature of -30° C in a fast-freezing apparatus with the following storage for 6-8 months, but small volume of production did not allow extending this technology of freezing to increase shelf life.

Thus, significant increase in practical terms of preserving the original quality of cheese is achieved by the use of low temperature freezing. In this regard, it is expedient to consider the issue of behavior of the main component water during the process of freezing and further low-temperature storage.

A large number of investigations is devoted to the study of the structure and properties of water, but until now there is no consensus on the structural model of water and patterns of its interaction with other substances are not explained. The main event in the development of the problem of water interaction was the classification of forms and types of relationships of moisture in materials created by Academician P,A, Rebinder [156].

Peculiarities of behavior of water and water solutions is explained by high energy of hydrogen bonds and especially O-H intramolecular communication. Thus, at low temperatures, the motion of H-O-H molecules is gradated, their structure changes with the formation of crystalline lattice [89, 138, 140, 141].

On the ground of numerous investigations V. Spiyes concluded that fast freezing prevents significant diffusion redistribution of moisture and soluble substances and promotes formation of small, evenly distributed ice crystals. The process of crystal formation, as a rule, changes proportionally to the rate of freezing as interfacial transition moves from the periphery to the center of a product. Microcrystalline structure is characteristic for the surface layers of the product. In this case, tissue structures and microstructure of food products remain intact [13, 49, 51, 69].

It is well known that the rate of crystallization determines the duration of impact of hypertonic solutions on the structure of protein causing greater or smaller degree of its denaturation. As a result, protein molecules lose their original properties and acquire new ones. There is no consensus among scientists on the impact of freezing rate on stability of proteins [13, 49, 69]. Some of them believe that in order to obtain a quality product freezing rate should be high, others think that freezing should be slow [2, 13, 49, 51, 69]. Reducing duration of impact of salt solutions on cheese protein structure during fast freezing reduces the degree of their changes. In addition, rational crystallization rates are different for different objects of freezing. Thus, microscopic investigations have shown that the structure remains better while maintaining high rates of freezing [49, 69].

While investigating the impact of temperature fluctuations on product quality during storage many scientists [2, 13] determined deterioration of products quality during continuous temperature fluctuations due to the course of physical and chemical processes in the crystal structure of ice. The reason for this was unstable durable properties of the crystalline lattice of frozen foods that are heterogeneous from the surface of an unfrozen product to its center, and their condition is determined by freezing rate.

Thus, preserving the quality of an unfrozen product throughout the shelf life is possible while maintaining a constant temperature in the refrigerator compartment [18, 55, 89].

1.4. Perspectives of the use of sunflower seeds kernel concentrate and gelatin in the composition of cheese structured semi-product

1.4.1. Characteristics of chemical composition of sunflower seed kernel and analysis of technologies of protein products of its processing

Taking into consideration current data of theoretical and research works made in Ukraine and abroad by the authors [53, 110-113, 122, 142, 173, 175], the possible ways of using products of processing sunflower seeds kernel oilcake, oilseed meal, flour and isolates were presented. All areas of industry, a range of combined food products and supplements that can be introduced to multicomponent products both of nutritional and functional purpose are marked out (Table 1.5).

Table 1.5

Food product or additive	Type of an additive from sunflower	Weight fraction of an additive					
Milk industry							
Soft thermal-acid cheese	Oilcake from sunflower seeds kernel	$1,5\%$					
Coagulation whey	Oilcake from sunflower	3,0%					
Meat industry							
Mincemeat for sausages, pelmeni (dumplings)	Modified protein additive from oilseed meal	$3-10%$					
Cooked sausage	Sunflower protein isolate	$2,1-2,2\%$					
Meat stewed paste	Meal of sunflower seeds kernel	$3-10\%$					
Mincemeat for cutlets	Meal of sunflower seeds kernel	$64 - 76%$					
Confectionery industry							
Sponge cake	Modified protein additive from oilseed meal	$3-10\%$					
Pralines	Oilseed meal from sunflower seeds of row motorial sot woight $\frac{2}{3}$ of moal woight	$10-15%$					

The use of products of processing sunflower seeds kernel in the composition of food products

 $-$ of raw material set weight, 2 – of meal weight

Scientists have [161] developed the technology of soft cheese obtained by thermal-acid coagulation with the use of oilcake of non-husk seeds cold pressing. Expediency of introducing oilcake to normalized or skimmed milk in the amount of 1.5% at temperature 50°С was determined. It was found that, in this case, weight fraction of protein in milk and vegetable mixture and cheese moisture increased, the strength of protein structure of cheese decreased, release of whey during cheese syneresis slowed down and that resulted in cheese yield increase.

The second type of oilcake from unhusked sunflower seeds was introduced in the amount of 3% to the coagulation whey with increased acidity to 120° T, then pasteurized at 75-80 $^{\circ}$ C with curing time of 5-7 minutes followed by filtration and addition of 8% dry whey.

Researchers [207] have developed modified protein additives from oilseed meal possessing high biological value, fat- and moisture-retaining ability in order to fortify meat and confectionery products with protein. Recipes of mincemeat with their use for producing sausages, dumplings and sponge cakes were developed.

Improvement of technological properties was conducted by enzymatic modification of oilseed meal for 30 minutes at temperature 20°С with compound of high proteinase activity obtained by germination of sunflower seeds at temperature 25°C and duration of 96 hours. Thus, three protein fractions isolated from oilseed meal had more than twice as much protein content compared to other factions.

Investigations have shown that enzymatic action of the compound caused a profound destruction of protein globules that contributed to the growth of relative biological value of protein additives by 10-50% and led to an increase in their fat- and moisture-retaining abilities by 30 and 65% respectively.

The method of cooked sausages production [132] includes the use in the mincemeat sunflower protein isolate in an amount of 2,1-2,2% of the raw material set weight and energetic additives.

It was proposed to use sunflower seed kernel in the composition of low calorie meat stewed paste intended for healthful nutrition. Meal of sunflower seeds kernel in the amount of 3-10% of the total weight of the mixture was introduced to the recipe mixture containing raw meat and additional components. The use of sunflower seed kernel meal conditioned obtaining the finished product with high organoleptic properties, increased nutritional and biological value, improved rheological characteristics.

Food concentrate [134] that can be used in the manufacture of mincemeat for cutlets, paste was developed. The authors suggested recipes of mincemeat for cutlets where food protein meal from sunflower seeds kernel in the amount of 64,0-76,0% of the total weight of food concentrate and buckwheat, vegetables and spices were used as food protein.

Among the world manufacturers Ukraine is ranked the third in croppage of sunflower seeds which is a traditional oilseeds and strategic raw material of Ukraine. Recently there has been an increase in sunflower croppage due to the expansion of acreage and yield increase by almost 30%. According to the data for 2006-2011, 5,32-6,77 million tons of sunflower were produced in Ukraine [56, 76, 77].

As of 2011 the register of sunflower cultivars included about 300 samples that differ on different grounds. Many cultivars and hybrids of sunflower are cultivated in Ukraine. Sunflower used as industrial raw material is classified into several types. Sunflower of linoleic and oleic types is distinguished by fatty acid composition of triacylglycerols. Sunflower of confectionary and oil types is distinguished by its purpose. In addition to these types, hybrid sunflower is separately distinguished [65, 145, 146]. In accordance with the state registration cultivars of high oleic direction should contain not less than 60.0% of oleic acid, of palmitic direction - not less than 7.0% of palmitic acid, of oil direction - not less than 48.0% of oil [23, 25, 216].

Protein complex of kernel is represented by spare proteins, proteinsenzymes and toxic proteins - inhibitors of proteolytic enzymes. Spare proteins of sunflower seed are located in complex aleurone granules that contain amorphous protein zone of non-crystalline protein and protein globoid formed by phosphoric phytin [57], catalytic proteins are included in the structure of biological membranes [90, 91]. Compounds of proteins with lipids and carbohydrates are also widely presented in sunflower seeds.

Spare proteins of sunflower seeds are represented by 11S- and 7Sglobulins, 2S-proteins that are the products of spare proteins breakdown into polypeptides, low-molecular globulins, albumins, some enzymes, inhibitors of proteolytic enzymes are present in smaller quantities [57, 88].

The main spare 11S-globulin of sunflower seed kernel is helianthine that consists of six spherical subunits in the form of a trigonal prism and has a molecular weight of about 300 kDa. Polypeptide chain of helianthine contains 10% of α-helix and 30% of β-conformation. 7S-proteins are composed of two or four types of subunits.

Toxic proteins belong to the low molecular proteins of albuminglobulin group with molecular weight of about 20 kDa [88].

Also, researchers [56] developed method of classification of samples by protein content in sunflower seed kernel in terms of absolutely dry raw material [57], where protein content varies from 14% to 34.0%.

Proteins of sunflower seed kernel contain all the essential amino acids, that are contained in 100 g of kernel more than in cow's milk (Table 1.6). According to the content of essential amino acids sunflower protein exceeds the seeds of many agricultural crops.

Table 1.6

Characteristics of amino acid composition of sunflower seed kernel		
	protein and cow's milk protein	

Fractional composition of sunflower seed kernel protein [99, 195] characterized by albuminovoyi, globulin, hlyutelinovoyi fraction. And in the protein composition of nuclei with high oil content dominates albuminova and low - globulin fraction [123-125, 128-135, 146] (Table 1.7)/

Table 1.7

Fractional composition of sunflower seed protein

A large part of carbohydrates such as pectin, hemicellulose (1.06...1.95%) is located in the cellular walls of sunflower seeds. Cellulose that is firmly linked to hemicellulose of cellular walls is present within 1.99...2.05%, The content of monosaccharides of glucose, fructose, galactose in the sunflower seed kernel is $0.31...0.48\%$ and oligosaccharides - 1.0...1.2%, of which 49...51% are sucrose, 32...36% - raffinose.

Ashy elements in sunflower seeds are 90% composed of macro elements that are in the form of oxides (% by weight of ash): $P_20 = 35,4-41,1$; $K_2O - 24,5-28,4$; Na₂ $0 - 7,4$; Ca $O - 7,6-17,0$; MgO – 12,3-17,9; Fe₂0₃ – 1,6. Trace elements are present in sunflower (mg/1 kg of dry weight): $B - 21.0$; Mn – 18.0; $Cu - 8.1$; $Zn - 52.5$. In the sunflower seed kernel there are 2.89...4.93% of ash [194].

Protein and protein-lipid products of processing sunflower seed kernel occupy significant place in the food products technologies. Depending on the technology that provides different concentration of protein in the obtained products, the latter are classified as follows (Table 1.8).

Semi-fat or defatted meal is obtained after thorough refining and grinding defatted seeds often with hexane. Flakes of defatted meal are sent to solvent stripping, then to drying and milling [57, 200].

Concentrate of sunflower seed kernel (CSSK) is defatted meal where part of simple and complex carbohydrates, mineral salts and other water-soluble substances is removed.

Table 1.8

Characteristics of the products of processing sunflower seed kernel and oilcake

Two groups of methods of obtaining concentrates are known - dry and liquid. Dry methods are based on air separation with the use of previously defatted and ground oil seeds as a result of differences in air flow by density, shape and size of components that compose sunflower seed meal (aleurone granules, splinters of cellular walls with cytoplasm that is adjacent to them, remnants of spherisomes' membranes, groups of whole and dilapidated cells and other components) [207-213].

Depending on the type of processing and type of cleansing solution liquid methods of obtaining protein concentrates have common purpose removal of carbohydrates, mineral salts and other water-soluble substances from the products of seeds processing.

The possibility of obtaining protein concentrates by liquid method appeared during development of methods of extracting oils from oil seeds with water.

The essence of the method lies in grinding refined seeds, mixing it with water, acid or other solution (such as alcohol) to form dispersion where protein is present in a soluble form. Then the dispersion is divided into solid and protein-lipid emulsion which, in turn, is divided into oil emulsion and protein substances that are precipitated from the extract then.

Obtained after drying protein substances are protein concentrates containing in their structure lipids (10-15%) and other substances. The logical development of this method in connection with the purpose of obtaining protein concentrates were methods of obtaining protein concentrates. Numerous varieties of methods of obtaining protein concentrates include the use of products from different stages of processing sunflower seeds.

Obtaining protein concentrates from sunflower seeds is associated with

difficulties determined by the presence of chlorogenic acid that causes the formation of undesirable color and reduces biological value.

Protein isolate from seeds is a highly refined from non-protein components product with protein content $\sim 90\%$. Scheme of protein isolates production consists of the following stages: extraction of proteins by alkaline value pH, further subsidence of protein at the isoelectric point, centrifugation, neutralization, drying and sterilization.

Analyzing the overall chemical composition of products of processing sunflower seed kernel (Table 1.9) it should be noted that protein content, on average, is in the meal - 43.3%, in the concentrate - 68.4%, and in the isolate - 86.3%.

Table 1.9

Protein		Energy value,					
products	Moisture	Carbo- Lipids Proteins Ashes hydrates					
Meal (semi-fat) or defatted)	8,1	43,3	38,9	6,1	2,1	1457,9	
Concentrate	5,7	68,4	18,9	3,8	1.2	1511,6	
Isolate	5.0	86,3	3,01	2.9	0,8	1592,1	

Characteristics of the average indices of chemical composition and energy value of products of processing sunflower seed kernel

In terms of biological value besides total protein content its quality that is characterized primarily by the content of essential amino acids is also very significant. As it is shown in the Table. 1.10 the amount of essential amino acids in the meal on average is 33.33%, in the concentrate - 32.49%, and in the isolate - 32.94%. This allows stating that the products of processing sunflower seed kernels have high nutritive and biological value.

Table 1.10

		Essential amino acids							
Protein products	aline	eucine –	soleucin −	$y\sin$ e ┙	ethion	hreonin ∸	a ptopha ╼	Phenylalanine	Ξ mo
Meal (semi-fat or defatted) 5,41 6,75 3,68 2,33 2,37						2,75			$1,19$ 5,83 31,31
Concentrate	15,37			$\left 6,83 \right 4,63 \right 2,23$	2,38 3,73				$1,17$ 6,10 32,49
Isolate			5,49 6,90 4,72 2,41		12,42	3,62	, 23	6,15	32,94

Characteristics of the content of essential amino acids of protein of products of processing sunflower seed kernel

The classical scheme of isolates production acquired many different options. The main changes relate to the preparation of oil meal for extraction and the choice of solvent and especially precipitator of proteins after extraction. Final stages of centrifugation, drying and sterilizing arte determined by improvement of technology and equipment for these processes of technology and equipment for these processes (supercentrifugation, vacuum-microwave drying, etc.). These changes contribute to increase in the yield and improvement of the quality of the isolated protein by its relatively constant content of 90-95%.

The raw material for obtaining protein products from sunflower seeds can be the seeds itself, semi-fat cake, defatted oil meal that are by-products of vegetable oils production that can be used for food purposes.

As it was stated, the actual task of improving lipid component of structured products based on cheese is a modification of its fatty acid composition. One of the effective ways to solve this problem is the use of vegetable oils which in comparison with butterfat have a number of advantages that are conditioned by the absence of cholesterol, the presence of a number of vitamins, high content of essential polyunsaturated fatty acids that promote excretion of cholesterol, condition the ability to reduce the risk of cardiovascular diseases and determine its own biological significance. Vegetable oils are quite common in the manufacture of structured products and they meet the requirements of a healthy diet most of all.

Comparative analysis of the fatty acid composition of vegetable oils which are perspective for use as part of a new structured cheese semi-product proved expediency of introduction of refined deodorized sunflower oil containing polyunsaturated fatty acids, particularly linoleic fatty acid (up to 75%), which refers to a group of essential acids, and oleic (up to 39%), which reveals the inherent effect of biotin. Besides, an important role in nutrition is assigned to tocopherols, phytosterols, carotenoids which are also present in sunflower oil. According to the data the content of vitamin E in sunflower oil is respectively 67/100 g of oil.

Thus, comparing the data obtained on the amino acid composition of cheese protein (Table 1.2) and concentrate kernel of sunflower seeds (CSSK) (Table 1.10) it can be stated that introduction of CSSK as well as refined deodorized sunflower oil to the composition of new structured cheese semiproduct will make it possible to effectively correct its amino acid and fatty acid composition, allow enriching it with other essential nutrients.

1.4.2. Analysis of the functional properties of gelatin

Gelatin - a compound that has both jellification and foaming properties due to its structure. It is water-soluble product of breakdown, destruction or cleavage of insoluble in water collagen fibers. Gelatin - is a gelling the active element of which is glutin. Protein product that is tasteless and odorless,

represented by a mixture of linear polypeptides with different molecular weight (50,000...70000 Da) and their aggregates with molecular weight up to 300000 Da.

Gelatin is a protein substance that is usually produced from high quality and mostly fresh collagen-containing raw material: skin, tendons, cartilage, bones of animals. Its purest form is derived from fish floats, called "fish glue". Depending on the method of extraction (acid and alkaline) two types of gelatin are classified [51, 156].

F. Hofmeister considers the process of formation of gelatin from collagen as hydrolysis during which collagen binds a molecule of water from formation of glutin. He considered collagen to be anhydride of glutin and considered transition of collagen into glutin to be the reverse process because when heating glutin to 130° C the product with properties that are different from those of glutin is formed: this product swelled in water with a lower degree and it transferred into solution very bad.

A.I. Zaydes, confirming that as a result of dry heating at a temperature 130...170° C gelatin (glutin) becomes insoluble not only in water but also in solutions of acids and alkalis, showed that loss of solubility cannot be considered as transformation into collagen because gelatin structure after heating differs from collagen structure even to a greater extent.

O. Henhross and E. Stiasin [51] believe that transformation of collagen into glutin should be considered as disaggregation that is splitting without breaking chains of the main valences.

A scheme [156] cleavage of collagen by which collagen under the influence of various substances changes in two directions – disintegration and re-formation. Disintegrated collagen processed witn hot water forms melting products (gelatin); re-formed collagen transforms into breakdown products that do not form gels.

Based on the works of S.A. Pavlov, S.I. Sokolov, N.V. Chernov glutin can be considered as composed from separate molecular chains of collagen. However, molecular chains of glutin contain more free carboxyl groups than molecular chains of collagen because during the process of previous treatment of collagen and under the influence of hot water on it, hydrolysis of amine groups with the release of ammonia takes place. So, it is consider that cleavage of collagen associated with the breach or rupture of intermolecular bonds within the chains without significant destruction of these bonds is the basic rule for converting collagen into gelatin.

Collagen is the main protein component of fibrous connective tissues that serve mainly for susception and mitigation of the tensile stress in mammals and fish.

The properties of collagen are determined by peculiarities of its composition. High content of amino acids (pyrrolidine cycles) leads to the formation of a large number of peptide bonds that develop with their

participation and hydrogen atoms. Creation of tertiary structure in collagen system with the help of disulfide bridges is impossible [156]. Exceptionally high content of such amino acids that break spiral structure in collagen gives reason to anticipate that collagen does not form spirals.

According to the amino acid composition collagen is unique among proteins. It is the only animal protein that contains a large number of oxyproline, glycine and proline. The presence of oxyclisine is also almost unique feature of collagen. Sulfur is contained very little in collagen. Cysteine is practically absent and methionine is the only sulfur-containing amino acid [51].

The structure of collagen fibers consists of three separate peptide chains, twisted in left-hand helix which, in turn, are twisted in right-hand superhelix [94]. Each amino acid residue of the chain is rotated around an axis at 120°, and three residues constitute one complete volution. Lead of each spiral is about 9 Å. Collagen chain mainly consists of four amino acid residues arranged in certain sequence: glycine-proline-oxyproline-glycine that are indicated Gly-Pro-Hypro-Gly [51, 156, 193].

Researchers mainly consider two models of collagen structure [153, 192], according to which glycine is in every third position of the polypeptide chain. That is why collagen peptide chains are represented as triplets: Pro-Hypro-Gly, Pro-X-Gly, X-Y-Gly. Where X and Y mark amino acid residues different from proline and oxyproline. The most significant difference between the models of collagen is the number of interchain hydrogen bonds. Models by Crick and Rich [192] presume the existence of one hydrogen bond to tripeptide unit. Ramanchandran's model presumes formation of two hydrogen bonds if the residue after glycine is not amino acid. Collagen in the native state exists only in the presence of water [51, 155, 193].

When heated in a solution collagen denatures. In this case transition from semicrystalline native state to amorphous, irregular occurs. The temperature of conformational transition of collagen depends on the content of amino acids.

The ways of conversion of monomer collagen into gelatin of different types are shown in Fig. 1.4. Arranged and fixed by means of hydrogen bonding configuration of monomeric molecule of collagen is easily destroyed by heating monodisperse collagen solution to 40° C in the presence of acid. Complete and sharp transition occurs in a narrow temperature interval during several minutes. Breakdown of the arranged molecular structure occurs in one of the following directions.

If there are no additional bonds between the chains then as a result of the breakdown three randomly rolled coils are formed by single peptide chains.

Otherwise, when two chains are linked by one or a large number of covalent bonds, denaturation leads to formation of two particles.

The third case - two or more cross-covalent bonds can link three

chains. Disorientation process destroys all traces of secondary structure, but the three chains cannot be separated and they are stored in the solution as a unity. This three-chain structure is called γ - component [155, 193].

It can be stated that any given preparation is heterogeneous due to intramolecular polymerization even if it is monodisperse in structure of tropocollagen core. Intramolecular heterogeneity occurs only when converting system to gelatin.

Gelatin consists of long chains of amino acids linked by peptide bonds. It occupies a unique place among other proteins. Peptide chains of gelatin take the configuration of a randomly rolled coil in water solutions at sufficiently high temperature [193].

Acidic and basic functional groups of amino acid side chains provide gelatin with properties of polyelectrolyte. These electrically charged parts of the chains are involved in regulating interaction of gelatin molecules with each other and with solvent molecules. They affect viscosity and other hydrodynamic properties of the system. Therefore, excessive and overall charges of a gelatin molecule, the nature of ionogenic groups and their internal allocation should be considered in order to understand and characterize gelatin system.

Gelatin consists of polymer chains built from amino acids of one left conformation and it has an elongated zigzag shape with directed in different directions side chains that alternate [51].

Hydrophobic side chains are located mainly on the one side of the area of the polypeptide chain and hydrophilic - on the other. When dissolved in water macromolecule takes the form of a helix. The ratio of the length of this helix to its width is within 1:15 ... 1:20.

In cold water gelatin does not dissolve, but swells absorbing 5 ... 50 fold amount of water with formation of stiff, elastic jells. Water absorbed during swelling is in two states: bound by colloidal particles' gravity force, this water evaporates badly from jells and it is called "water of hydration"; water in free state located between gelatin molecules is called "water of swelling." The latter easily evaporates during gelatin drying. Gelatin forms chemical compounds with acids, alkalis and salts [51].

When heated swelled gelatin transforms easily into solution, so the process of swelling can be considered as an initial stage to dissolving. At the first stage of this process (during hydration of gelatin) compression of the system of gelatin - water (contraction) with release of heat takes place. Maximum heat of swelling 1g of dry gelatin is 139 ... 150 J.

Swelling goes on very fast initially, then gradually it slows down and finally absorption of water by gelatin stops. As the temperature increases the rate of gelatin swelling increases slightly due to the acceleration of water diffusion into swelling gelatin. The degree of gelatin swelling is largely dependent on the pH. According to Fisher's data acids that increase gelatin swelling are located in the following sequence:

 $HCI > HNO₃ > CH₃COOH > H₃SO₄ > H₃BO₃$

In dilute alkalis gelatin swells less than in acids. During adding neutral salts to acids and alkalis swelling decreases, sometimes it is lower than in water. Influence of salts is explained by the joint action of anions and cations. Cations and anions that reduce gelatin swelling in acids or alkalis are located in the following order:

> Cations – Fe²⁺> Cu⁺> Sr²⁺> Ba²⁺> Ca²⁺> NH₄⁺> Na⁺> K⁺ Anions – $PO_4^3 > SO_4^2 > CH_3COO > NO_3 > Br > Zn^2$

Gelatin has amphoteric properties. Electrochemical nature of gelatin solutions as well as solutions of other protein substances depends on the concentration of hydrogen and hydroxyl ions in solution. At a certain pH value of solution a gelatin molecule contains the same number of positive and negative charges. This pH value corresponds to the isoelectric point of gelatin.

At the isoelectric point gelatin molecules are not transported to either the anode or the cathode. Isoelectric point of gelatin derived from material treated with lime suspension is in the range of 4.7...5.0. Isoelectric point of the native collagen is in the range of pH 6.5...7.8. This sharp transition of isoelectric point is conditioned by cleavage of ammonia mainly due to the hydrolysis of amide groups of residues of aspargic and glutamic acids as a result of processing collagen-containing raw material with lime suspension. As a result of ammonia cleavage carboxyl groups are released:

$$
\text{RCONH}_2 + \text{HOH} \xrightarrow{\text{Ca(OH)}_2} \text{RCOOH} + \text{NH}_3
$$

Amide groups are retained during the use of the acid method of treatment of collagen-containing raw material. Isoelectric point of gelatin derived by acid method varies between pH of 8.0...9.0. At the isoelectric point of gelatin some quality indicators such as viscosity, swelling, temperature of jells melting, transparency have the minimum value and the ability of gelatin solutions to clotting (coagulation), sedimentation - the maximum value [51].

At temperature below 40°C conformational transformation of gelatin macromolecules from static coil into collagen-like helix occurs in solutions of gelatin. As a result of a large number of intermolecular bonds aggregates of macromolecules i.e. particles of new lyophilic phase are formed from supersaturated solutions of gelatin. Their accumulation further causes occurrence of strong disperse structures. Linking particles of new polymer phase with formation of contacts leads to emergence of bulk structure of gel which is characterized by solid-like mechanical properties [51].

The nature of links participating in the formation of three-dimensional pattern of gels in solution of gelatin has not been studied enough so far. There

are various controversial views. Most researchers believe that the main role is played by the interaction between polar groups (salt-like links) [51], while others prefer hydrophobic links [155], some argue the possible existence of hydrogen bonds [193]. It is also believed that all the above mentioned types of links are involved in gel formation [220]. V.N. Izmaylova, V.A. Pchelin, Samir Abu Ali conducted a number of studies to confirm the latter assumption as the most likely one [155]. The authors studied the effect of concentration, pH, ionic salts and urea on melting temperature of gelatin gels. As a result of experiments, it was determined that at low concentrations of gelatin up to 2.0% links between functional groups play a significant role during the process of gel formation.

In gels of average concentration (from 2.0 to 20.0%) hydrogen links also play a significant role, and in gels with a concentration more than 20.0% contacts are also provided by hydrophobic links.

In the work [51, 155] the authors investigated the structure of gels during transition helix-coil. As a result of studies it was determined that at a temperature of 36° C and higher only gelatin molecules exist in the state of a static coil. During cooling to 20° C the speed of helix formation increases, that is associated with the formation of hydrogen links that bind the helix at this temperature. At a temperature 17..20°C decrease in the movement of molecules and segments occurs, which complicates the formation of helical conformations, and also at these temperatures most of the gelatin molecules transforms form a static coil form into a helical conformation. The authors also determined that the transformation from a helix conformation to a static coil conformation for gelatin molecules does not depend on whether the molecules are located in the solution or participate in the formation of gels structures.

According to the classification of P.A. Rebinder cross-linked systems can be classified into two types: coagulation (reversible thixotropic) with weak structural links and condensation-crystallization (irreversibly destroying) - with strong links [155].

Gels - cross-linked polymer solutions - are elastic solids and they are formed at concentrations of 1% and higher. In terms of rheology gels are viscoelastic fluids.

In food gels polymer molecules are not linked by crossed and covalent links. Instead, they are held together by a combination of weak intermolecular forces: hydrogen links, electrostatic forces, the forces of Van der Waals and hydrophobic interactions. Crossed links are not point interactions, they have large segments of two or more polymer molecules usually in clearly defined structures, so-called transition zones. In fact, gel formation is a process of forming transition zones (Figure 1.1).

To study the properties of food gels it is necessary to understand how transition zones, i.e. corresponding molecular structures and intermolecular forces that ensure their stability, are formed. There is a high degree of interaction: separate molecular forces are very weak, but together they form a stable crossed link. These crossed links are not permanent but free as they are continuously broken and re-formed again [51].

Gel formation mechanism probably involves nonspecific interactions. At the same time, hydrophobic links, hydrogen links and electrostatic forces are equally important.

Fig. 1.1 – Principal diagram of gel structure

Currently, there are two explanations for the chains association mechanism leading to the formation of gelatin gels: crystallization (model of bichromatic micelles) or local association of chains due to conformational transition of globule-coil, and restoration of structure without further aggregation and formation of microcrystals.

This is confirmed in the works [51, 155]. During gel formation process metastable collagen-like structures are formed. Bradbury and Martin [155] mark out three basic processes as occurring in

the system during gel formation: formation of asymmetric chain elements, establishment of interchain contacts, increase in gelatin systems ordering.

The first of these three processes is intramolecular, the latter two depend on the intermolecular interactions. Gel formation involves the formation of segments with collagen conformation and inter-segment stabilization by hydrogen links. Interchain hydrogen links are formed between asymmetric chain elements that have an internal ordering, providing strong interchain contacts that lead to the formation of three-dimensional pattern of gel.

Thus, as a result of cooling solution of gelatin, at first, intramolecular rearrangement of the part of peptide chains into collagen folding occurs. Formation of folds similar to polyglycine ones, stabilized by hydrogen interamide and carbonyl groups also occurs in the formation of collagen folds.

Gelatin gels are formed reversibly during gelatin solution cooling. At temperatures below 40° C conformational transition of a macromolecule of gelatin from static globule into collagen-like helix occurs in gelatin solutions. As a result of a large number of intermolecular links, aggregates of macromolecules, i.e. particles of a new lyophilic phase are formed from supersaturated solutions of gelatin.

Their accumulation causes further occurrence of strong disperse structures. Coalescence of particles of a new polymer phase with formation of contacts leads to the appearance of the bulk structure of gel, solid-like, that is

characteristic of mechanical properties [51, 155, 156, 193].

The authors [155] have shown that in very diluted gelatin gels transitional zones are completely intermolecular, at least - at the early stages. Results of the study of gel formation kinetics confirm this conclusion [155, 196, 198]. The reaction is close to the third order dependence on the concentration at the early stages of gel formation, decreasing to the second order in the course of the reaction. The average number of amino acid residues is 142. This represents about 16 turns in the triple helical structure of collagen.

Gel formation is a kinetic process, the higher the speed of increase in gels strength is, the higher concentration of protein in the system is. The speed of gel formation of gelatin is the largest in the isoelectric state and it decreases during transition to acidic or alkaline area. The speed of structure formation and the value of the marginal strength of gelatin gels increases with decreasing temperature. The strength of gelatin gels structure increases with increasing concentration.

The most important functional feature of gelatin is the formation of highly thermo-reversible gel with a melting point that is at the level of a human body temperature (less than 37° C) - lower than that of pectin, carrageenan, agar that provide less elastic and more brittle gels.

Resistance of gels to thermal destruction increases when gels are formed slowly or hardened gel was preheated before melting, and in the case when the temperature of chilled gel is increased at a speed slower than 12^o C per 1 h.

These data indicate that not all crossed links are equally stable and that exposure at higher temperatures of slow gel formation contributes to a more stable crossed links due to the weaker ones. Rapid cooling causes more chaotic formation of weak and less organized branched areas. This confirms the importance of thermal prehistory of aggregates or gel of gelatin for their stability.

Temperature lowering results in a rapid increase in the number of helixes; principal amount of helixes (80%) appears at an early stage of gel maturation in about an hour, and further increase in the number of helixes is significantly slower.

The process of gel formation in water gels of gelatin at 20° C practically finishes in 7 days. In this case, 75-85% of the process takes place in 24 hours [51].

CHAPTER 2

SCIENTIFIC SUBSTANTIATION OF TECHNOLOGICAL PARAMETERS OF OBTAINING STRUCTURED SYSTEM BASED ON NONFAT THAWED CHEESE

2.1. Analytical substantiation of the technology of cheese structured semi-product based on nonfat thawed cheese with the use of sunflower seed kernel concentrate

New food products made on the base of milk protein more and more take on a food market and occupy a prominent place in the diet of the population.

Against the background of the current crisis in the dairy sector in Ukraine that is manifested in the growth of the raw milk deficit, cheese in particular, as well as under conditions of negative changes in the structure of diet of Ukrainian population and development of essential nutrients, the issue of finding alternative sources of protein raw material, providing restaurant enterprises with it and product expansion due to the creation of new products with higher nutritional value is currently important.

Typically, cheese is stored at temperature 2...6° C, packaged in cans, boxes - no longer than 36 hours; in case of packing in parchment - no longer than 3 days; in case of packing in consumer packaging from polymeric materials, laminated foil and plastic wrap - no longer than 7 days [164].

Taking into consideration short periods of storage and due to seasonality of provisions and decrease in the amount of milk for supplying processing facilities with cheese, it should be reserved by freezing. Modern technologies of refrigeration processing and storage of food products have a wide range of advantages in comparison with other methods of preservation. They significantly maintain high quality of cheese, minimize changes in nutritional value and organoleptic characteristics, as well as significantly reduce the weight loss of the product during storage, increasing the terms of storage by times [89, 104, 108].

Sunflower seed kernel has large reserves of protein and rich chemical composition. It is a leading culture of Ukraine and it is traditionally used in many food technologies. A number of products of kernel processing should be marked out - meal, concentrates, isolates, hydrolysates, textured protein that are obtained after extraction of oil with the aim of concentrating a valuable component - protein. Market analysis of food products involving protein products of processing sunflower seed kernel determined (Table 1.1) that its range is very narrow. It should be mentioned that protein products of processing sunflower seed kernel, particularly concentrates, are not used in technologies of structured products based on cheese at all. The main deterrent of introducing these technologies is the lack of scientific grounds for their use.

We have obtained concentrate of sunflower seed kernel from huskless sunflower seed kernel on a special experimental stand (Figure 2.1) by method of cold pressing at a temperature not higher than 50° C. It was assumed to create cheese structured semi-product recipe composition of which included the following raw material as a carrier of nutritional value and functionaltechnological components: nonfat cheese thawed – as a protein base, obtained concentrate of sunflower seed kernel – as a protein fortifier, a mix of vegetable oils – as a fat component and instant gelatin - as a structure-forming agent.

Thus, the development of scientifically substantiated technology of cheese structured semi-product with realization of extensive functionaltechnological properties of its components will enable the adoption of new ways of introducing this raw material to the structured products based on nonfat cheese with controlled structural-mechanical properties, nutritional value, amino acid and fatty acid composition.

On the basis of the above mentioned prerequisites there was developed a working hypothesis of the creation of cheese structured semi-product. The proposed working hypothesis presupposes the application of basic principles that are as follows:

- the use of nonfat cheese thawed as a protein base;
- introduction of sunflower seed kernel concentrate as a carrier of functional- technological substances (protein), sunflower oil deodorized as a source of polyunsaturated fatty acids, edible vegetable fat as an additional fat component and a structure controller;
- the use of instant gelatin as a structure-forming agent;
- providing conditions for converting milk protein into a soluble state;
- providing high aggregative and kinetic stability of the emulsion system;
- providing predetermined structural-mechanical properties of the finished product;
- creating a product safe in terms of hygiene and microbiology.

In view of the above mentioned principles we have developed a model of innovation strategy (Figure 2.1) of creating cheese structured semi-product.

The basis of the innovative strategy is the development of the technology of cheese structured semi-product based on nonfat cheese thawed with the use of sunflower seed kernel concentrate of as an additional source of protein substances, realization of functional-technological properties of animal and plant proteins, providing high emulsifying capacity and stability of the obtained system, and as its structure formation with the help of gelatin with predetermined structural-mechanical properties.

Within the framework of the developed innovative strategy, determination of the technological parameters that provide preparation of milkplant raw material, conversion of cheese protein into a soluble state, obtaining the emulsion system as the basis for the finished product is important.

Fig. 2.1. Model of innovative strategy of cheese structured semiproduct development with the use of sunflower seed kernel concentrate: 1 calcium bridge; 2 - submicelle (A); 3 - submicelle (B); 4 - submicelle (C); 5 surfactants; 6 - emulsified oil; 7 - emulsified moisture; 8 - sunflower seed protein; 9 - hydration shell of submicelle.

The peculiarity of the technology of cheese structured semi-product is the use of nonfat cheese thawed with addition of sodium citrate to it that provides the necessary ion exchange. Thus, due to hydrolysis of sodium citrate the destruction of "calcium bridges" of milk protein occurs, hydration increases and it converts into a soluble state.

Adding gelatin to that protein system will contribute to the complex formation and creation of the disperse medium for the further emulsification of the mix of vegetable oils (Figure 2.1).

Sunflower seed kernel concentrate by dispersing of which a complex polydisperse colloid emulsion system is formed, is added to the obtained emulsion system based on the complex of nonfat cheese proteins and gelatin. Surfactants in the formation and stabilization of such emulsion can be watersoluble proteins of the sunflower seed kernel concentrate, cheese and gelatin albumins and pseudoglobulins.

Thus, common use of milk and plant raw material on condition of the use of specific scientifically substantiated technological operations can provide technological system with specific properties different from their simple mixture, forming a three-dimensional pattern structure that can be used to stabilize heterogeneous systems.

On the basis of the presented hypothesis and innovative strategy (Figure 2.1) there was developed a model of the technological system (Figure 2.2) of obtaining cheese structured semi-product based of nonfat cheese thawed with the use of sunflower seed kernel concentrate.

The model of technological scheme includes the following subsystems: E – "Preparation of components": D – "Obtaining protein basis"": C – "The formation of emulsion system"; $B -$ "The formation of disperse emulsion system"; $A -$ "Obtaining cheese structured semi-product" within each of which a clearly defined purpose is realized.

The developed models (Fig. 2.1, 2.2) allow to strategically determine the necessary theoretical and experimental studies for their implementation by the most cost-effective way.

The next stage was focused on conducting the necessary analytical and experimental work, both within each of the subsystems and within the technological scheme as a whole.

2.2. Substantiation of the content of main recipe components

2.2.1 Substantiation of the content of thawed cheese as a protein basis

The quality of cheese is influenced by the packaging weight and material of a packaging unit, method of freezing, temperature and duration of low-temperature storage, method of thawing.

The above was the basis for the study of the results of the process cooling treatment cottage cheese, comprising the steps of: prepacking and packaging, freezing, storage, thawing.

In accordance with the regulatory document the weight of nonfat cheese thawed of customer-size packaging must be not more than 0,5 kg in case of packaging in the parchment paper and polyethylene film, we accepted the weight of 0.2 kg, and in blocks packaging we accepted the weight of 6,0 kg.

We have investigated nonfat cheese with fat concentration of $\leq 2\%$. Cheese was prepacked and packaged in brickets weighing 0.2 kg in parchment paper and put into boxes with liners made of polyethylene film and in blocks weighing 6.0 kg, packaged in polyethylene film. Then, they were frozen, stored and thawed (Table 2.1 ... 2.5).

Modes of freezing, storage and thawing were selected as follows (Table 2.1).

Slow freezing. At that type of freezing cheese at temperature of $4\pm 1^{\circ}$ C is transported to the chamber with air temperature minus $8\pm1^{\circ}$ C, after lowering the temperature of the product to minus $8\pm1^{\circ}$ C it is transported to the next chamber with the temperature of minus $18\pm1^{\circ}$ C, and then to the next one with the temperature of minus 25 ± 1 ° C. Freezing is free convection method to the average final temperature under minus $8 \pm 1^{\circ}$ C, $-18 \pm 1^{\circ}$ C, $-25 \pm 1^{\circ}$ C. The freezing speed is $(0.5...2)$ ° C/h.

Table 2.1

Title	Temperature
Slow freezing	Staged decrease of temperature from $4\pm1^{\circ}$ C to: $I - -8 \pm 1$ °C; II - -18 ± 1 °C; III - -25 ± 1 °C
Fast freezing	-25 ± 1 °C
Storage	$-8\pm1^{\circ}$ C; $-18\pm1^{\circ}$ C; $-25\pm1^{\circ}$ C
Slow thawing	$+1015^{\circ}$ C to the temperature in the product of $0\pm 1.0^{\circ}$ C
Fast thawing	$+4045^{\circ}$ C to the temperature in the product of $0\pm 1.0^{\circ}$ C
Two-stage thawing: the first stage; the second stage	20 ± 1 ° C to the temperature in the product of $0\pm 1.0^{\circ}$ C, 4045° C to the temperature in the product of $0\pm1.0^{\circ}$ C

Modes of freezing, storage and thawing nonfat cheese
Fast freezing. Packed cheese at temperature of $4\pm 1^{\circ}$ C is transported to the refrigeration chamber with the temperature of minus $25\pm1^{\circ}$ C. The freezing speed is (10.0 ± 0.5) ° C/h.

Storage. Pre-frozen cheese is stored at the temperature not higher than minus $8\pm1^{\circ}$ C. This mode provides transportation of thawed cheese in the refrigerated vehicle. The temperature is minus $18\pm1^{\circ}$ C and minus $25\pm1^{\circ}$ C. These temperature modes are used at food production enterprises.

Slow thawing, acceptable temperature range is $+10...15$ ° C to the temperature inside the product of $0\pm 1,0^{\circ}$ C during 72×60^{2} s,

Fast thawing. At air temperature of $+40...45^{\circ}$ C during $(6...12) \times 60^2$ s to the temperature in the product of $0\pm 1,0^{\circ}$ C. The temperature level is within the range of proteins denaturation, raising temperature above this range is impractical.

Two-stage thawing. First, at air temperature of $20\pm2^{\circ}$ C to the temperature in the product of $0\pm 1.0^{\circ}$ C, then at $40...45^{\circ}$ C to the temperature in the product of $0\pm 1,0^{\circ}$ C during $(9...12) \times 60^{2}$ s.

While conducting experiments on technological process of refrigeration treatment (Table 2.2, 2.3) samples of cheese obtained by acid-rennet method were taken. Cheese obtained by this method was chosen from the perspective of its larger production compared to the acid one. In addition, cheese produced by acid-rennet method compared to the cheese produced by acid method is distinguished by a higher content of free amino acids [72], that is conditioned by duration of fermentation and influence of rennet enzyme which has proteolytic action [66, 67] and provides flexible and homogenous texture.

Thus, samples were taken - nonfat cheese where fat content is not more than 2% and protein not less than 20% and titrated acidity is within 170...250°T.

From Table. 2.2 and 2.3 it is clear that the type of packaging and weight of prepacking affect the value of losses of cheese weight after freezing, storing and thawing. By packaging the product in polyethylene film, thawed cheese losses are reduced. The duration of the process is conditioned by the small surface of heat transfer of thawed block at larger weight.

Change of cheese weight is observed at change of storage temperature. Thus, at the temperature of minus $8\pm1.5^{\circ}$ C weight losses during slow thawing of cheese packaged in blocks were $17.9\pm0.7\%$ and at the temperature of minus $25\pm1.5^{\circ}$ C, under the same conditions - 15,0 \pm 0,7%. Analyzing the results of the table. 2.2 and table. 2.3 and on the basis of the observations during the experiments as well as degustation evaluation it can be mentioned that the value of the temperature affect the morphological structure that shapes the quality of the product.

The freezing temperature stability is also of great importance. The lower the temperature, according to the statement of the author [89] minus 25 ± 1.5 ° C – the more spontaneously more centers of ice crystallization are

formed, that almost does not cause significant changes in cheese texture. It is possible that during thawing small, evenly distributed ice crystals, humidity is allocated throughout the whole weight. Thus, it can be assumed that small ice crystals that are formed inside cheese granules, do not destroy them significantly.

Table 2.2

					\cdot		\circ			
	Index	Value depending on the type of packaging and net weight								
	Type of packaging	film parchment paper								
	Net weight, kg	0,2					6,0			
	temperature.	$\left\{ \pm \right\}$	$-18+1$	-25 ± 1	$\frac{8+1}{2}$	-18 ± 1	-25 ± 1	$\frac{1}{2}$	$-18+1$	$-25 + 1$
Storage 1	duration. mon.		12							
eight losses unethod of న awi ∕ɗ ≷	slow									$10,3\pm0.5$ $8,6\pm0.4$ $7,5\pm0.3$ $9,0\pm0.4$ $7,9\pm0.3$ $6,8\pm0.3$ $14,8\pm0.7$ $13,7\pm0.6$ $12,9\pm0.6$
	$\frac{1}{2}$ fast	$4,3\pm0,2$ $4,2\pm0,2$ $3,9\pm0,2$ $4,2\pm0,2$ $3,0\pm0,2$ $3,6\pm0,2$ $5,6\pm0,3$							$5,0+0,2$	$4,6 \pm 0.2$
	\equiv two stage	$4,6\pm0,2$ $4,2\pm0,2$ $3,8\pm0,2$ $4,4\pm0,2$ $3,4\pm0,1$ $3,9\pm0,2$ $6,2\pm0,3$							$5,7\pm0.2$	$4,9 \pm 0,2$

Results of the research of the technological process of refrigeration treatment of nonfat cheese by fast freezing method

It should be emphasized that in order to preserve the quality and reduce the loss of cheese weight one of the main roles in the technological process of refrigeration treatment is alloted to the ways of thawing.

Table 2.3

Results of the research of the technological process of refrigeration treatment of nonfat cheese by slow freezing method

After fast freezing and storage, thawing by fast method to $(6...12)$ × $60²$ s allows reducing losses up to 3.6...4.6%; two-stage method of thawing reduces losses to 3.9...4.9%, the duration of this method does not significantly differ from the fast method; slow method of thawing with duration of up to 72 \times $60²$ s c also allows reducing cheese losses to 6.8...12.9% (Table 2.4).

After slow freezing and storage, thawing by the slow method with duration of up to 72×60^2 s results in maximum weight losses of cheese $(17.4...21.8\%)$.

Table 24

Influence of technological stages of the process of refrigeration treatment on the weight losses of nonfat cheese

Due to slow method of freezing and temperature above minus $18\pm1^{\circ}$ C centers of water crystallization are formed unevenly that promotes the formation of large crystals, during melting process of which while cheese thawing granulated and crumbly structure with uneven allocation of moisture throughout the mass is formed and its partial free release from the product occurs with decrease in water-retaining capacity (Figure 2.2).

Figure 2.2. The dependence of the water-retaining capacity of nonfat cheese on the duration of storage at the temperature of minus 25° C.

The obtained results studying the effective viscosity, water-retaining capacity, shear boundary stress indicate that after fast freezing, storing and fast

thawing the above mentioned indexes decrease. Thus, the effective viscosity is reduced by 9 \ldots 13 Pa \times s, water-retaining capacity is reduced by 8 \ldots 12% (Figure 2.3), and the shear boundary stress is reduced by 27 ... 49 Pа (Table 2.5). In our opinion, this is associated with a decrease in aggregative stability of cheese protein.

These results are aligned with studies [88], from which it can be concluded that strength of cheese structure decreases during refrigeration treatment.

Thus, freezing, storing and thawing is accompanied by converting water that is contained in cheese into ice crystals that affects thermophysical and structural-mechanical properties. Breaking moisture bonds with proteins leads to the deterioration of its hydrophilic properties [139]. Decrease in the effective viscosity of cheese (Table 2.5) that characterizes the rheological properties is probably associated with the destruction of the structural pattern of cheese protein complex.

Table 2.5

Index		Value depending on the type of packaging, net weight and temperature								
			parchment paper		film					
		0.2 kg						6.0 kg		
		-8 ± 1.5	-18 ± 1.5	-25 ± 1.5	-8 ± 1.5	-18 ± 1.5	-25 ± 1.5	-8 ± 1.5	-18 ± 1.5	-25 ± 1.5
Effective viscosity,	before freezing			71.4±2.5 71.4±3.5 71.4±3.5 71.4±3.5 71.4±3.5 71.4±3.5 71.4±3.5 71.4±3.5 71.4±3.5 71.4±3.5						
$Pa \times s$	lafter thawing			$ 60,1\pm3,0 59,2\pm3,0 58,3\pm2,9 59,1\pm2,9 59,3\pm2,9 57,9\pm2,8 58,3\pm2,9 59,0\pm2,9 59,4\pm2,9 59,2\pm3,0 59,3\pm3,0 59,4\pm3,0 59,3\pm3,0 59,4\pm3,0 59,3\pm3,0 59,3\pm3,0 59,3\pm3,0 59,3\pm3,0 59,3\pm3,0 59,3\pm3,0 59,3\pm3,0 59,3\pm3,0$						
Water- retaining	lbefore freezing			$(61,1\pm3,0)$ $(61,1\pm3,0)$ $(61,1\pm3,0)$ $(61,1\pm3,0)$ $(61,1\pm3,0)$ $(61,1\pm3,0)$ $(61,1\pm3,0)$ $(61,1\pm3,0)$						
capacity,%	lafter thawing			49.8±2.4 49.8±2.5 50.0±2.5 48.2±2.4 49.1±2.4 49.2±2.4 48.1±2.4 48.4±2.4 48.9±2.4						
Shear boundary	before freezing	$472 + 23$	468 ± 23	484±24	496±25	479±24	468 ± 23	470 ± 23	463 ± 23	481 ± 24
stress, Pa	after thawing	437±22	430 ± 21	435 ± 21	441±22	428±21	420 ± 21	430 ± 21	$418 + 21$	440 ± 22

The results of studies of the refrigeration treatment effect on the effective viscosity, water-retaining capacity, shear boundary stress of nonfat cheese

During refrigeration treatment changes of quality occur in cheese (Fig. 2.4...2.7). They depend on the temperature, type of packaging, weight and method of cheese freezing and thawing [2, 68, 125, 191]. Organoleptic properties of the latter is affected by the biochemical changes in butterfat that usually develop in two directions: hydrolytic breakdown and oxidation. At low temperatures oxidative processes prevail that results in fat rancidifying[140].

Changes in butterfat are determined by controlling formation of free fatty acids (acid number) and primary products of oxidation (peroxide number) [92-102, 140].

Test samples were taken before freezing, during freezing, after thawing and during storage. It was established that the acid number of cheese fat packaged by weight of 0.2 kg during the entire period of storage has higher indexes in comparison with nonfat cheese packaged by weight of 6.0 kg (Figure 2.4).

Figure 2.4. Change of the acid number of cheese fat during slow freezing (C), storage (B), fast thawing (A) at temperature: $1, 2 - 8 \pm 1^{\circ}$ C; $3, 4 18\pm1^{\circ}$ C; 5, 6 – -25 $\pm1^{\circ}$ C (- cheese weight of 6 kg, --- cheese weight of 0.2 kg)

From these data show that a slow freezing cottage cheese weighing 0.2 kg at a temperature of minus 8 ± 1 ° C. acid number increased by 23.0%, with - 18 ± 1 ° C - 16.6%, less 25 ± 1 ° C - 11.2%.

During fast freezing the acid number of cheese fat weighing 0.2 kg changes to a less degree; at the temperature of minus $8\pm1^{\circ}$ C by 4.3%, at minus $18\pm1^{\circ}$ C – by 3.5%, at minus $25\pm1^{\circ}$ C – by 2.9% (Figure 2.5).

It was determined that during storage changes of these indexes depend on the temperature of storage and speed of freezing. Thus, in the fast frozen samples after 6 months of storage at the temperature of minus 18 ± 1 ° C the acid number of cheese fat increased by 20.8%. In the slow frozen samples - at the temperature of minus $18\pm1^{\circ}$ C – by 44.1%. Increase in oxidative processes in the slow frozen cheese is the result of biochemical changes that go on during the process of freezing and increase in the amount of destabilized fat [139] that is subject to oxidation processes to a greater degree.

With decreasing storage temperature to minus $25\pm1^{\circ}$ C biochemical changes of fat slowed and its acid numbers in slow frozen cheese increased by 32.6% after 6 months of storage. This index is increased only by 12.9% in fast frozen cheese.

Figure 2.5. Change of the acid number of cheese fat during slow freezing (C), storage (B), fast thawing (A) at temperature: $1, 2 - 8 \pm 1^{\circ}$ C; $3, 4 -18\pm1^{\circ}$ C; 5, 6 – $-25\pm1^{\circ}$ C (- cheese weight of 6 kg, --- cheese weight of 0.2 kg)

Peroxide numbers of nonfat cheese fat during fast freezing practically did not changed (Figure 2.7) and during slow freezing they increased (Figure 2.6).

Figure 2.6. Change of peroxide number of cheese fat during slow freezing (C) , storage (B) , slow thawing (A) : 1, 2 - cheese, freezing and storage at the temperature of $-8\pm 1^\circ$ C; 3, 4 – at the temperature of $-18\pm 1^\circ$ C; 5, 6 - at the temperature of -25 \pm 1° C (— cheese of 6 kg weight, --- cheese of 0,2 kg weight)

At storage temperature of minus $8\pm1^{\circ}$ C the course of biochemical processes of milk fat is more intense. After 6 months of storage peroxide number of nonfat cheese fat increased by 2.4 times during fast freezing and by 2.8 times during slow freezing.

At storage temperature of minus $18\pm1^{\circ}$ C in fat of fast thawed cheese of 6 kg packaging peroxide number remained in an acceptable range for 10 months and at the temperature of minus 25 ± 1 °C – for more than 12 months.

We also studied the influence of the type of packing and packaging on the quality of the product thawed by fast way (blocks of 6.0 kg weight packed in film). Thus, intensive increase in peroxide number occurs in cheese packed by 0.2 kg, that is associated with higher oxidative changes of milk fat due to increased surface contact of the product with air oxygen. In addition, it is more expressed in cheese at storage temperature of minus 8±1° C. Peroxide number of cheese during 6 months of storage at the temperature of minus 25 ± 1 ° C in blocks of 6.0 kg weight increases by 1.28 times, in brickets of 0,2 kg weight by 1.92 times.

Based on the conducted experiments it was determined that the intensity of oxidative changes of cheese fat depends on the method of freezing and thawing, storage modes, type of packing and weight of packaging.

Figure 2.7. Change of peroxide number of cheese fat during fast freezing (C), storage (B), fast thawing (A) at the temperature: $1, 2 - 8 \pm 1^{\circ}$ C; 3, $4 - 18 \pm 1^{\circ}$ C; 5, $6 - 25 \pm 1^{\circ}$ C (– cheese of 6 kg weight, --- cheese of 0.2 kg weight)

During slow freezing the speed of formation of primary oxidation products is more intense, causing effects on the process of milk fat oxidation during further storage.

In fast frozen and fast thawed cheese oxidation processes of fat during storage are less intense and remain in an acceptable range of -0.03%, for nonfat cheese of 6.0 kg weight at the temperature of minus $25\pm1^{\circ}$ C up to 12 months and for cheese of 0,2 kg at the temperature of minus $25\pm1^{\circ}$ C up to 8 months.

The scheme of technological process of the refrigeration treatment of cheese shown in Fig. 2.8, allows storing the product frozen up to 12 months with a minimum loss of weight of the product with quite high organoleptic and quality indices.

Figure 2.8. The scheme of technological process of the refrigeration treatment of nonfat cheese thawed.

Subsystem $D - \alpha$ Preparation of cheese for freezing». To do this cheese is packaged in parchment paper and plastic wrap weighing not more than 0.2 kg, or in film not more than 6.0 kg.

Subsystem $C - \langle$ Freezing». Cheese is fast frozen to the temperature of minus $25\pm1^{\circ}$ C. The process of freezing continues until obtaining a stable core temperature.

Subsystem $B - \alpha$ Storage». Cheese is stored at the temperature of minus 18 ± 1 ° C and minus 25 ± 1 ° C for 12 months. It should be emphasized that in the premises where the product is stored there should not be fluctuations of the air temperature, it must be stable. Fluctuations of the temperature lead to recrystallization of small crystals into larger ones and to undesirable effects (deterioration of organoleptic properties and reduction of physical and chemical parameters and, as a result, deterioration of quality).

Subsystem $A - \alpha$ Thawing». Fast thawing reduces losses and preserves the quality of the product. Modes of its conducting: $t=40$... $45\pm1^{\circ}$ C for $(6...12) \times 60^{-2}$. Two-stage thawing is divided into two stages:

- thawing at the temperature of $20 \pm 1^{\circ}$ C for $(4,5...6) \times 60^{-2}$ s;

- thawing at the temperature of 40 ... $45\pm1^{\circ}$ C for $(9...12)\times60^{\circ}$ s.

2.2.2. Characteristics of functional and technological properties of sunflower seed kernel concentrate

One of the types of plant protein raw material used in food technologies is sunflower seed kernel possessing high biological value. According to the data of authors [72, 88], protein of sunflower seed kernel is the closest to the standard – albumen, in comparison with the other plant proteins.

The sunflower seed kernel contains from 25 to 57% of plant lipids consisting of glycerides, fatty acids and some carotenoids. Also hey contain: proteins (up to 28%), carbohydrates (up to 32%), tannins (up to 1,8%), phytin (up to $2,0\%$), acids (chlorogenic, citric, dihydroxysuccinic) $[56, 57, 75, 88]$.

During the processing of sunflower seeds, besides oil, up to 35% of oilcakes are received, which contain 30…36% of protein, 5…9% of fat, 20% of carbohydrates, pectin – 20%, phytin -3,5%, minerals, water, and fat-soluble vitamins.

The authors suggested a new method of getting sunflower seed kernel concentration at a special equipment – test-bed (fig. 2.9) for the reception of oil from pure kernel without husk by means of cold pressing at temperature not above 50° C that resulted in the reception of two new products: oil and sunflower seed kernel concentration.

Test-bed consists of a working chamber 4, a batcher 5 with theca 6 above the chamber for the delivery of seeds, working chamber has the carrier-grinding zone 7 and squeezing zone 8 equipped with heating elements. At the end of a working chamber there is matrix 10 with the holes 11 for the husks outcome, and channel 12 in a shaft of a hollow squeezing worm for the outcome of oil. Actuating device of the installation

consists of a gear motor 1 and shaft coupling 2, connected with the worm shaft 3. Inside the working chamber there is the hollow squeezing worm 8 (fig. 2.10).

Fig. 2.9. Test-bed for the reception of the sunflower seed kernel: 1 gear motor; 2 – coupling; 3 – worm shaft; 4 – working chamber; 5 – container; 6 – theca; 7 - carrier-grinding zone; 8 – squeezing zone; 9 – heating elements; 10 – matrix; 11- holes for the husk outlet; 12 – channel for the oil outcome.

Fig. 2.10. Profile of the working chamber of the installation: $1 -$ working chamber; 2 – longitudinal knives; 3 – theca for seeds; 4 – carrier-grinding zone; 5 – squeezing zone; 6 – matrix; 7 – holes for the outgo of husks; 8 – hollow worm; 9 – heating elements; $10 -$ worm shaft; $11 -$ driving end of the shaft; 12 outlet end for oil; 13 – shaft coils; 14 – grinding nozzle; 15 – pressing holes; 16 – channel for the oil outlet

First electric heating elements 9 are switched on. The side of the working chamber 1 heats to the predetermined temperature (fig. 2.10). After starting the

actuating gear, worm 8 begins rotating. The seeds are conveyed via theca 6. The seeds are captured by the flight 13 of the worm 8, and moved in the interturn space of the worm along the cavity of the working chamber 1, becoming more compact, and deforming during pressing in the result of decreasing the step of the worm's flight screw and reduction of interturn space. Fixedly locked to the interior side of the working chamber 1, longitudinal knives 2 together with the worm 8 restrain the pressed seeds from scrolling, thus guarantee longitudinal relocation of mass in the carrier-grinding zone 4 of the working chamber 1.

In the interterm space where the group of grinding heads 14 is mounted, the deformed particles of seeds are ground. Pressing during the worm 8 rotation and heating, the pressed mass evolves oil, which comes inside the worm through the back hole, and then to the channel 16 of the hollow shaft 10, and flows out from the press into the containers. The husks are pressed through the holes 7 of matrix 6 in a husk receiver. Rectification of oil to the central zone assists creating of gas-air mixture in the interior surface of the working chamber, which gives heat off, and then outcomes. More oil is pressed in the result of additional grinding and mixing of the pressed mass if additional grinding heads 14 are mounted in interturn space of squeezing zone 5. Heating elements 9 have external layer of thermal insulation.

It is established (table 2.7) that organoleptic indices of the sunflower seed kernel concentration allow effectively use it as the ingredient of cheese structured semi-product on the basis of lactic defrosted cheese due to high dispensability, neutral or light smell of sunflower oil and neutral taste. 18 amino acids are identified quantitatively (table 2.8). The total amount of essential amino acids equals 32,54%, that allows characterize sunflower seed kernel concentrate as a product of high biological value.

Table 2.7

Index	Characteristics of the index
Form	Fine powder with size of the particles ≤ 50 micrometer
Color	White with light gray shade
Smell	Neutral or slight smell of sunflower oil
Taste	Neutral

Characteristics of organoleptic indices of sunflower seed kernel concentrate

It is seen in the table that the existing limiting acids – isoleucine, leucine and lysine, are overloaded with other amino acids.

Biological value of proteins of sunflower seed kernel concentrate was evaluated by the calculated value of amino acid score, discrepancy coefficient of amino acid score (DCAS), biological value (BV), and coefficient of protein utility (U) (table 2.9).

Table 2.8

	гиппо аста сотрожной ог рговет от записомет зеса кегиет сопсени авс
Name of amino acid	Amount, mg/100g
Total amount of amino acids	48785
Essential amino acids:	15874
Valine	2494
Isoleucine	1783
Leucine	3193
Lysine	1824
Methionine	1002
Threonine	2274
Tryptophan	856
Phenylalanine	2438
Nonessential amino acids:	32911
Alanine	2204
Arginine	4329
Aspaginic acid	4339
Histidine	1344
Glycine	2646
Glutamic acid	9824
Proline	2775
Serine	2035
Tyrosine	1398
Cystine	1017

Amino acid composition of protein of sunflower seed kernel concentrate

Table 2.9

Indices of biological value of sunflower seed kernel concentrate

An extremely important index of biological value of protein is both the presence of all these amino acids and their balanced state [4]. Index of "threonine" was calculated for the evaluation of its levels (table 2.10).

Table 2.10

Balanced state of amino acid composition of protein of sunflower seed kernel concentrate

Analysis of the correlation by "threonine" index demonstrated that protein of the sunflower seed kernel concentrate is limited by methionine.

Chemical identifier of the sunflower seed kernel concentrate are presented in table 2.11, from which it is seen that protein in the concentrate is found within the limits $45...50\%$, fat – up to 10% , moist content fluctuates within the range $6.3...6.9\%$, and about 2.7% of cellulose.

Table 2.11

Characteristics of chemical indices of sunflower seed kernel concentrate

The investigations of water and fat retention capacities, fat-emulsifying capacity demonstrate that the sunflower seed kernel concentrate is a good emulsifier retaining water and is a fat retaining component (table 2.12).

Thus, the experiments carried out with the elaborated sunflower seed kernel concentrate proved it to be a highly effective food adjunct with a wide spectrum of functional and technological features. It allows us recommending it to be used in the recipe of the cheese structured semi-product based on defrosted sour-milk cheese, which will enrich it with plant proteins and fatty acids.

Characteristics of technological indices of sunflower seed kernel concentrate

2.2.3. Substantiation of the choice of a structure-forming agent

Most of the combined products, among which there is a cheese structured semi-product based on defrosted sour-milk cheese, with the account of a large spectrum of chemical composition and nature of the ingredients, are complex heterogenous systems with a unitary internal structure and common physicalchemical features. Food adjuncts added to the recipe as the ingredients during preparation are used for the stabilization of texture, and creation of the required structural-mechanical properties.

Stabilization of the received emulsion system is an important aspect for heterogenous products. Stabilization is perfomed through the introduction of substances regulating strength, structural viscosity of adsorption interphase layers, and influence the changes of structural-mechanical properties: viscosity, temperature of structuring, melting, etc. [51, 81, 156, 168].

Main demands to the stabilizers:

- compatibility with the dispersed phase and dispersion medium;

 $-$ regulation of the rate of structuring:

 $-$ the capability to preserve the product during its storage without synergism and its suitability to cooking;

 $-$ the capability of granting the necessary structural-mechanical properties;

 $-$ the absence of toxic and allergic reactions;

 $-$ low price and availability.

Safety, harmlessness, low viscosity (fig. 2.11), and high level of jellification were the major criteria for the choice of a structure-forming agent during the investigations. Gelatin and sulphatic polysaccharides: agar (vegetable gelatin), carrageenan, furcellaran [51] are successfully used in foodstuffs out of all existing structuring agents.

Table 2.13 presents strength, the temperatures of structuring and melting. Data analyses proves that the strength of jellies of structure-forming agents depend on their chemical composition, concentration, sources and their nature. The concentrations of kappa carrageenan - 2.0% , agar - 1.0% . furcellaran – 2.0% , and instant gelatin – 3.0% , which are usually used for

foodstuffs manufacture, were taken as minimal rational concentrations of jelling agents [156, 193].

Table 2.13

	\sim		. .	
Name of structuring agent	Gel strength, g	Structuring temperature, t _{str.} , \circ	Melting temperature, t _{mel.} , \circ	$t_{\text{mel}}-t_{\text{str.}}$ $\rm ^{\circ}C$
Kappa carrageenan $(1,0\%$ solution)	450 ± 18	$20,0+0,4$	$59,0 \pm 0.9$	$38,0 \pm 1,5$
Agar $(1,0\%$ solution)	375 ± 17	$33,0+0,5$	$76,0 \pm 0.9$	$43,0 \pm 1,4$
Furcellaran $(2,0\%$ solution)	115 ± 6	$22,0+0,4$	$58,0 \pm 0,8$	$36,0 \pm 1,2$
Instant gelatin $(3,0\%$ solution)	345 ± 16	$18,0+0,2$	$33,0+0,3$	$14,0\pm0,5$

Functional-technological properties of structuring jellies

Increase of gel concentration promotes the growth of the number of intermolecular links, which are mostly hydrogenous. Despite a great energy of hydrogenous connection (20 kJ/mol), the increase of concentrations of structureforming agents increases strength, temperature of structure formation, melting, and effective viscosity that is demonstrated as the compaction of the gel grid. It is clear that functional-technological indices are strongly marked, which influences structural, mechanical, and organoleptic characteristics.

The research of functional-technological properties of the jellies of structuring agents (table 2.13) was carried out according to the strength of the structure 335…355 g of the analogue – cheese product Feta Lissima. It was specified that the strength of jellies $335...355$ g is secured by instant gelatin with the concentration 3,0%. The similar strength can be secured by cappacarrageenan, agar and furcellaran, though structural-mechanical features of the ready product worsen.

The figure 2.11 shows that phase transition liquid-gel occurs at maximal temperature at the level 33° C – for agar, 22° C – for furcellaran, 20° C – for cappa-carrageenan, 18° C – for gelatin.

The gel of gelatin possesses the lowest temperature of gel formation and melting.

Fig. 2.11 shows that the data of effective viscosity are lower in comparison with the similar indices of sulfite polysaccharides.

It is known [168] that gelatin is used as a structuring agent for milk products. It coincides with the milk proteins much better, taking into account their similar nature.

It is determined (fig. 2.11) that at a temperature above 80° C, viscosity of the solutions of gelling agents equal: for cappa-carrageenan - $3,1\pm0,2\times10^{-3}$ Pa×s, for agar - 1,7 \pm 0,1 \times 10⁻³ Pa×s, for furcellaran - 3,7 \pm 0,2 \times 10⁻³ Pa×s, for

gelatin - 2,4 \pm 0,1 \times 10⁻³ Pa \times s.

Fig. 2.11. Dependence of the effective viscosity of the solutions of structuring agents on temperature: $1 - \text{cappa-carrageenan} - 1.0\%$, $2 - \text{agar} -$ 1,0%, 3 – furcellaran – 2,0%, gelatin – 3,0%.

Table 2.14

		Deformation, $104m$			Relative	
Name, concentration	E_0	$E_{\rm M}$	$E_{\rm rem.}$	plasticity, %	springiness, $\frac{0}{0}$	elasticity, $\%$
Cappa-carrageenan $(1,0\%$ solution)	2,74	4,29	0,75	17,5	63,9	36,1
Agar $(1,0\%$ solution)	3,78	4,75	1,63	35,5	79,9	20,1
Furcellaran (2,0% solution)	8,81	14,21	4,59	32,3	69,0	31,0
Instant gelatin $(3,0\%$ solution)	3,40	4,00	1,60	40,0	85,0	15,0
Cheese product Feta Lissima	3,50	4,15	1,74	41,9	84,3	15,7

Characteristics of rheological indices of gels and a test sample

It is seen from table 2.9 that by its functional properties instant gelatin with the concentration 3% better corresponds the requirements of the

technology under development. By the momentary, maximal, residual deformation, and relative plasticity, springiness, and elasticity, it is the closest to structural-mechanical characteristics of Feta Lissima cheese product, which was chosen for testing.

The gels of cappa-carrageenan and agar contain a lot of aggregates of molecular spirals. In a great measure they perform elastic and plastic features. In a less degree they simultaneously demonstrate elastic properties, which are considerable characteristic to the gels of gelatin.

It is evident that the power of the interaction of substances composing the gel adds them specific mechanical features – plasticity, elasticity, viscosity, strength, which objectively characterize their structure [137].

Moisture-retention property of protein was investigated by binding free moisture, adding dry gelatin and influencing pH protein basis through the introduction of sodium citrate (fig. 2.12) for the provision of thermal stability of protein basis of a cheese structured semi-product, and for the determination of rational concentrations of instant gelatin as a structuring agent and sodium citrate as pH regulator.

Graphs analysis (fig. 2.12) showed that at the increase of sodium citrate concentration from 1 ± 0.1 to 3 ± 0.1 %, the value of VRC protein basis by the content of instant gelatin $1\pm 0.1\%$, $2\pm 0.1\%$, $3\pm 0.1\%$ respectively increases at 22%, 33% and 40%.

Fig. 2.12. Dependence of moisture-retaining ability of protein basis on sodium citrate concentration by the content of instant gelatin: 1-1%; 2-2%; 3-3%

So, it is possible to suppose that with the account of the characteristics of functional-technological properties (strength, structure-forming temperature, melting, the process of viscous flow, jelling agent concentration) and structuralmechanical parameters (immediate deformation, maximal, remaining, relative plasticity, elasticity), instant gelatin as a structuring agent for the model system of a cheese structured semi-product on the grounds of defrosted lactic cheese is rational.

2.2.4. The choice and substantiation of fatty component

Milk fat is a main fatty component of milk products including paste-like soft, solid, structured products. It adds creamy taste and consistence [50, 166].

It is known that considerable reduction of milk and its high production cost in Ukraine created deficit of milk fat used for the manufacture of milk products. Besides, new economic market conditions made the producers search for the less deficient, cheaper fatty raw material with a simultaneous raise of biological and nutritive value. It resulted in a wider use of different fats and their compositions for partial or full substitution of milk products. Deodorized sunflower oil, the use of which allows to raise nutritive value and organoleptic parameters of milk products is one of such fats. Vegetable fat, the consistence of which depends on the temperature, and which can influence structuralmechanical characteristics of a product is the other among such fats.

Sunflower oil contains a large amount of important essential polyunsaturated fatty acids and vitamin E, which play an important role in a human body [24]. Nutritive vegetable fat within the cheese structured semiproduct will permit to regulate its structural and mechanical characteristics.

To specify the correlation of nutritive vegetable fat and refined deodorized sunflower oil, which are added into the recipe of the cheese structured semi-product, their influence on effective viscosity was studied (fig. 2.13).

Fig. 2.13. The dependence of effective viscosity on the temperature and correlation of oil and nutritive vegetable fat: 1 – nutritive vegetable fat; 2 – fat: oil – $2:1:3 - \text{fat: oil} - 1:1:4 - \text{fat: oil} - 1:2:5 - \text{oil}$

The use of refined deodorized oil and nutritive vegetable fat as a fatty component [8, 25, 69, 124, 139, 207, 210] allows both widen the assortment, balance the content of polyunsaturated fatty acids, and allows additionally regulate texture characteristics of a ready product. There are very little essential acids in milk fat: linoleic acid is contained within the limits of $1.5...4.5\%$. linolenic - $0.2...0.21\%$. At the same time refine deodorized oil contains ~60% of linoleic acid.

It was found (fig. 2.13) that effective viscosity of fatty component oil: nutritive vegetable fat in correlation 1:1 in a greater degree approached the viscosity of gelatin gel at the concentration 3%, which was chosen as a structuring agent and would not sufficiently influence the process of emulsifying.

It is known that emulsification is the process occurring with the energy wastes, so, it is reasonable to perform it in the zone with low viscosity. So, we take the concentration of fatty component around 30% at temperature $30...40^{\circ}$ C. As previous investigations demonstrated, rational correlation of oil to nutritive vegetable fat in fatty component is 1:1.

Emulsifying ability (fig. 2.14) of milk-vegetable protein base of a cheese structured semi-product was studied by means of finding the point of phases inversion during the emulsification, changing concentration of one of the major components in the recipe at temperature $30...40^{\circ}$ C with the mixer frequency $25 \pm 2c^{-1}$.

Fig. 2.14. Dependence of emulsifying ability of protein base (refrigerated nonfat lactic cheese) on concentration of main components: 1 – sodium citrate (C_1) ; 2 - gelatin (C_2) ; 3 – sunflower seed kernel concentrate (C_1) .

It was established (fig. 2.12) that at the addition of the concentration of sunflower seed kernel in within the range of 3…7,0% helps to increase emulsifying ability to 12 vol.un. of oil, evidently, as a result of the increase of the content of surface-active substances. Addition of sodium citrate to protein base within the limits from 1 to 3% helps to raise emulsifying ability to 22 vol.un. of oil, evidently, as a result of pH increase. Addition of gelatin to protein base within the limits from 1 to 5% results in a slight decrease of emulsifying ability from 2 vol.un. of oil that is connected with hydration changes of major protein of refrigerated lactic cheese, as a result of the viscosity increase.

It is established that mass particle of non-broken phase of the emulsion system (table 2.15) depends on fat content, components concentration.

 $\mathbb{N}_{\mathbb{Q}}$ The contents of components Fat volume,% Aggregate stability,% Kinetic stability,% 1 | 2 | 3 | 4 | 5 20 | 47.8 | 78.6 30 64,4 87,5 1 sodium citrate 2%, sunflower seed

kernel concentrate 5% Nonfat lactic cheese 20%, gelatin 3%, kernel concentrate 5% 50 85,5 94,6 20 | 66,9 | 84,5 30 75,8 89,2 2 sodium citrate 2%, sunflower seed

kernel concentrate 5% Nonfat lactic cheese 30%, gelatin 3%, kernel concentrate 5% 50 93,6 97,8 20 75,7 88,4 30 81,6 93,5 40 90.7 97.3 3 sodium citrate 2%, sunflower seed Nonfat lactic cheese 40%, gelatin 3%, kernel concentrate 5% 50 95,9 98,6 20 61.5 82.6 30 73,4 86,3 4 sodium citrate 2%, sunflower seed

kernel concentrate 3% Nonfat lactic cheese 30%, gelatin 3%, kernel concentrate 3%, 50 89,7 95,1 20 | 80,1 | 88,5 30 88,6 92,4 5 sodium citrate 2%, sunflower seed
 $\begin{array}{|c|c|c|c|c|c|c|c|} \hline 50 & 60,0 & 92,4 \\ \hline & 40 & 90,2 & 95,5 \\ \hline \end{array}$ Nonfat lactic cheese 30%, gelatin 3%, kernel concentrate 5% 50 | 95,3 | 96,7 20 88,6 92,3 30 94,4 95,1 6 sodium citrate 2%, sunflower seed

kernel concentrate 7% and 40 95,0 97,2 Nonfat lactic cheese 30%, gelatin 3%, kernel concentrate 7%, 50 96,8 98,1

Indexes of model emulsion stability of a cheese structured semi-product

Table 2.15

Table 2.15 continued

	$\overline{2}$	3	$\overline{4}$	5
		20	72,6	90,1
	Nonfat lactic cheese 30%, sunflower	30	81,4	93,2
7	seed kernel concentrate 5%, sodium	40	88,7	94,4
	citrate 2%, gelatin 1%	50	90,5	96,5
		20	85,2	84,6
8	Nonfat lactic cheese 30%, sunflower seed kernel concentrate 5%, sodium	30	91,5	90,0
	citrate 2%, gelatin 3%	40	92,3	92,5
		50	95,1	96,3
		20	90,1	80,0
9	Nonfat lactic cheese 30%, sunflower seed kernel concentrate 5%, sodium	30	95,2	84,5
	citrate 2% , gelatin 5%	40	95,5	90,1
		50	96,3	94,6
		20	56,4	84,1
10	Nonfat lactic cheese 30%, sunflower seed kernel concentrate 5% gelatin	30	67,6	90,6
	3% sodium citrate 1%	40	83,5	92,5
		50	89,8	95,6
	Nonfat lactic cheese 30%, sunflower	20	73,7	90,4
11	seed kernel concentrate 5% gelatin	30	81,4	94,5
	3% sodium citrate 2%	40	89,8	96,6
		50	92,4	97,8
		20	82,9	93,4
12	Nonfat lactic cheese 30%; sunflower seed kernel concentrate 5% gelatin	30	88,5	97,5
	3%, sodium citrate 3%	40	93,8	98,5
		50	95,9	98,8

As it is seen from table 2.15, during the addition of fat component – oil and nutritive vegetable fat in correlation 1:1 within the limits 20 to 50% to the sample containing 5% of the concentrate of sunflower seed kernel aggregate stability of the created emulsion system grows within the limits $801 \quad 99.3\%$ kinetic stability increases within the limits 88,5…99,6%.

In the sample containing 3% of gelatin aggregate stability of the created emulsion system grows within the limits 73,7…98,3%, kinetic stability increases within the limits 84,6…99,6%.

In the sample containing 2% of sodium nitrate aggregate, stability of the created emulsion system raises within the limits 85,2…98,8%, kinetic stability increases within the limits 90,4…99,7%.

To investigate stability of the emulsion system of a cheese structured semi-product the diagrams were constructed by standard methods (fig. 2.15- 2.18). It is done by means of measuring the dependence of aggregate and kinetic stability on fat volume.

Fig. 2.15. Dependence of the emulsion system stability on concentration of fatty component with sodium citrate in the recipe of a cheese structured semi-

Fig. 2.16. Dependence of the emulsion system stability on concentration of fatty component with the amount of the concentration of sunflower seed kernel
in the recipe of a cheese structured semi-product, %: $1-3$; $2-5$; $3-7$.

Fig. 2.17. Dependence of the emulsion system stability on concentration of fatty component with lactic cheese in the recipe of a cheese structured semi-
product, %: $1 - 20$; $2 - 30$; $3 - 50$

Fig. 2.18. Dependence of the emulsion system stability on concentration of fatty component with gelatin in the recipe of a cheese structured semi-product, $\frac{96}{6}$: $1 - 1$; $2 - 3$; $3 - 5$

Analysis of graphs (fig. 2.15…2.18) showed that addition of concentration of sunflower seed kernel in the amount $5\pm0.5\%$ to protein base of a cheese structured semi-product (refrigerated nonfat lactic cheese) results in the increase of aggregate stability to 88,6% and kinetic stability to 92,4%. Adding of instant gelatin in the amount $3.0\pm0.2\%$ results in the growth of aggregate stability to 91,5% and slight fall of kinetic stability to 90,0%.

So, the investigations proved that fat content of a model emulsion system of a cheese structured semi-product can be within the range from 20 to 50% at the maintenance of kinetic stability. At the stage of emulsification cutoff it is reasonable to introduce the concentration of sunflower seed kernel within the limits $5.0\pm0.5\%$, that promoted the increase of emulsifying capacity with the refrigerated nonfat lactic cheese $5.0\pm 0.5\%$ to 12 of vol.un. oil. Rational concentration of sodium citrate in protein base 2,0% that guarantees the largest emulsifying capability 22 ± 0.1 vol.un. Also it is necessary to introduce gelatin as a structuring agent with a high moisture-connecting capability for the provision of high aggregate emulsive stability of cheese structured semi-product besides heat treatment.

2.3. Investigation of structural-mechanical characteristics

Investigation of the dependence of structural-mechanical indexes of model system of the cheese structured semi-product on the concentration of main ingredients (fig. 2.19, 2.20, 2.21; table 2.16-2.18) was carried out in the following way: concentration of one component was changed at the fixed value of the others. Investigations proved rational values of the ingredients of the cheese structured semiproduct: sunflower seed kernel concentrate– 5% : gelatin – 3% : oil -15%; nutritive vegetable fat – 15%.

Fig. 2.19. Dependence of the deformation of load and relaxation of model system of a cheese structured semi-product on gelatin concentration: $1 - 1\%$; $2 - 3\%$; $3 - 5\%$; 4 – check

Fig. 2.20. Dependence of the deformation of load and relaxation of model system of a cheese structured semi-product on the content of sunflower seed kernel concentrate: $1 - 2.5\%$; $2 - 5\%$; $3 - 7.5\%$; $4 - \text{check}$

The most stable to pressing tension are the samples with the content of sunflower seed kernel concentration 7.5%, with general deformation 3696×10^{-3} ; with gelatin content 5% with general deformation 4496×10^{-3} ; vegetable fat 30% with general deformation 4032×10^{-3} , that is conformed with organoleptic indexes of a semi-product.

Fig. 2.21. Dependence of the deformation of load and relaxation of model system of a cheese structured semi-product on fatty component concentration: $1 - oil$, $2 - oil$: nutritive vegetable fat $- 1:1$, 30% ; $3 - neutrite$ vegetable fat – 30%; 4 - check

As it is seen from creep carves (fig. 2.19, 2.20, 2.21), the most fluent are the samples with the content of sunflower seed kernel concentration 2,5% with general deformation 9680×10^{-3} ; with gelatin content 15 with general

deformation 8440×10^{-3} ; and with the content of fatty component 30% with general deformation 8496×10^{-3} .

Table 2.16

Structural-mechanical parameters of model system of a cheese structured semi-product with various gelatin concentration

Table 2.17

Structural-mechanical parameters of model system of a cheese structured semi-product with different amounts of sunflower seed kernel concentrate

Table 2.18

		Fatty component	
Name of the parameter	Oil	Oil:nutritive vegetable fat, (1:1)	Nutritive vegetable fat
Reversible deformation, 10^{-3}	8016	4688	3552
Nonreversible deformation, 10^{-3}	480	1344	480
General deformation, 10^{-3}	8496	6032	4032
Voltage, Pa	1249	1249	1249
Flexibility, Pa^{-1} , 10^{-3}	0,0068	0,0048	0,0032
Conditionally instantaneous elasticity module, Pa	222,4	312,2	494,1
High-elastic module, Pa	520,4	1815,5	1219,8
Plastic viscosity, Pa \times s, 10 ⁶	9,4	3,4	9,4
Relation of reversible deformation to general	0,94	0,78	0,88
Viscosity of elastic aftereffect, $Pa \times s$, 10^5	1,9	9,4	6,3

Structural-mechanical parameters of model system of a cheese structured semi-product with 30% fatty component

Tables 2.16-2.18 of modules dependence on concentration of the ingredients demonstrate that conditionally instantaneous elasticity module within the range of sunflower seed kernel concentrate 2,5 … 7,5% increase at 79,6%, 192,75…940,55 Pa respectively; within the range of gelatin concentrations 1…5% parameters grows at 39,7%; within the range of vegetable oils concentration 15…30% conditionally instantaneous elasticity module reduces at 28,8%, for fatty component (oil: nutritive vegetable oil) at such parameters increases at 36,8%.

Decrease in gelatin contents by more than 1% causes sufficient reduction of elasticity module and results in the increase of the structure fluidity as a result of weakening spatial carcass of structuring agent and destruction of slice structure. Reduction of oil amount over 15% causes increase of elasticity module and leads to structure compression, maybe due to the strengthening of moisture links with protein because of its lack in the system.

The raise of gelatin contents over 30% causes sharp increase of elasticity module that results in the structure compression due to the strengthening of a spatial carcass of a structuring agent's action, and transition of slice structure to fragile, strong. The raise of the contents of sunflower seed concentration over 7,5% and the contents of vegetable fat over 15% causes sharp increase of elasticity module that leads to the formation of hard structure. The raise of oil contents in the recipe over 15% causes decrease of elasticity module that results in viscous structure, maybe because of reduction of intermolecular connections of protein with oil, as a result of hydrophilic hydrophobic interactions; increase of its emulsive ability through the reduction of free moisture in the recipe.

2.4. Investigation of moisture losses

It is found that the process of all samples decay occurs endothermally in two stages. On each of DTA curve two endo-effects are fixed, the position of which for each sample is different (fig. 2.22) [6].

 Each stage characterizes the corresponding process, which occurs in a cheese structured semi-product under the influence of temperature. The first stage characterizes the end of melting process, the other characterizes the structure destruction because of large water losses in the result of its intense evaporation.

Maximal temperature values characterizing the stages of thermal decay of the samples are presented in table 2.19.

Comparative analysis of thermal analytical curves (TG, DTG, DTA, T) samples the model system of a cheese structured semi-product with the diverse contents of sunflower seed kernel concentration showed that the rate of the process of samples decay by the contents of 3% sunflower seed kernel concentration was much higher and both on the first stage (the beginning and the end of melting process) and on the second stage (the process of a structure decay)

At all stages of experimental samples decay the mass is lost in the result of water evaporation. The largest losses of mass are characteristic for the sample with 3% sunflower seed kernel concentrate and at the first stage achieve 4.1% (8.2 mg), at the second stage they can achieve 16.2% (32.4 mg). The mass losses for the samples with the contents of 5% and 7% sunflower seed kernel concentrates are much smaller and respectively are at the first stage 2,8% (5,6 mg) and $2,4\%$ (4,8 mg), at the second stage they are $11,0\%$ (22,0 mg) and 10,2% (20,4 mg). It means that they are thermostable.

Table 2.19

Fig. 2.22. Derivatograms of the model system of a cheese structured semi-product by the contents of sunflower seed kernel concentration: a) – 3%, b) – 5%, c) – 7%, and by gelatin contents: a_1) – 1%, b_1) – 3%, c₁) – 5%. T – heating curve; TG – mass variation curve; DTG – the curve of mass variation rate; DTA – differential curve of heat capacity thermal analysis

The received thermographic data prove that the contents of sunflower seed kernel concentrate in a model system of a cheese structured semi-product increases energetic connection of water molecules with protein, reducing water activation energy. The sample of a structured 3% cheese semi-product concentrate possesses bigger activation energy among the investigated samples that demonstrate its smaller thermo-stability (fig. 2.23).

Fig. 2.23. Logarithmic dependence of mass losses of a model system of a cheese structured semi-product on temperature with the diverse contents of sunflower seed kernel concentrate: $1-3\%$; $2-5\%$; $3-7\%$.

The capability of evaluating the values of energy activation with the help of differential thermos-gravymetry (DTG) and temperature (T) under survey is experimentally proved: the weight of a cheese structured semi-product is 200 ± 2 mg, samples' heating rate is 5 ± 1 degrees/min in air medium of the oven under nonisothermal conditions, thermal junction is placed into the sample.

It is determined that the process of decay of the model system of a cheese structured semi-product is carried out endothermally during two stages with the mass loss after water evaporation. The most thermostable are the samples with the contents of 5% and 7% sunflower seed concentration. The most thermostable are the samples with the contents of 3% and 5% gelatin (fig. 2.24).

The value of the activation energy of thermal treatment process, which characterizes the value of moisture binding by the protein of the model system of a cheese structured semi-product with various contents of sunflower seed kernel concentration: 3%, 5%, 7%, that for non-isothermal conditions of investigating equals: 24,61; 28,17; 30,52 J/mole.

The received thermographic data prove that gelatin contents in the model system of a cheese structured semi-product raises energy connections of water molecules with protein decreasing water activation energy. The sample with 1% contents of gelatin has more activation energy among the investigated samples that demonstrates its smaller thermo-stability.

Fig. 2.24. Logarithmic dependence of mass losses on temperature of the model system of a cheese structured semi-product with different contents of gelatin: $1 - 1\%$; $2 - 3\%$; $3 - 5\%$.

The possibility of evaluating activation energy by means of the curves of differential thermos-gravymetry (DTG) and temperature (T) under survey: the weigh is 200 ± 2 mg, heating rate of the samples is 5 ± 1 degrees per min. in the air environment of the oven under non-isothermic conditions, thermal junction is in the sample.

2.5. Investigation of complex formation of the ingredients of a cheese structured semi-product model system

2.5.1 Studying effective viscosity and activation energy of the solutions

An important technological ability of liquid systems is viscosity, which determines their behavior in the process of cooking and packing of various food products. This ability is predetermined by cohesion between the molecules and is liquid resistance to its movement under the external influence.

There are two processes in the system at any rate of deformation: destruction and renewal of the structure. Viscosity is a cumulative characteristic feature describing the equilibrium state between these processes in a stable flow.

Previous researches (chapter 2.1) allowed determine rational concentration of nonfat thawed lactic cheese in a cheese structured semi-product.

The following rational concentrations of nonfat thawed lactic cheese were determined – within $50.0 \pm 5\%$, sunflower seed kernel concentrate -5,0 \pm 0,5%, soluble gelatin – 3,0 \pm 0,2%, sodium citrate – 2,0 \pm 0,2%.

Quantitative amount of sodium caseinate in 50,0±5% of nonfat thawed lactic cheese, which constituted 7,7 g, was recalculated for further experimental investigations in model systems.

Viscosity is an important component of rheological characteristics of nutrients' solutions. The value of effective viscosity depends on intermolecular

interactions (fig. 2.25). Three types of intermolecular interactions can be distinguished in water solutions of proteins and polysaccharides: molecular interactions between water molecules, macromolecules and water, and similar and different macromolecules, which are found in the solution.

Figure 2.25 demonstrates that the solutions containing only protein, have two linear sections with different activation energies. Reduction of E proves that intermolecular bonds in the solutions under research correspond molecular (or Van-der-Vaalsivsky) forces, but not chemical ones. The bonds weaken with raising the temperature, and at temperature 50…60° С they get specific minimal value depending on the nature of the dissolved substance.

Figure 2.25 Dependence of the effective viscosity of model solutions on temperature: $1 - 7.7$ g sodium caseinate, 97,0 ml water; $2 - 3.0$ g gelatin, 97,0 ml water; $3 - 3.0$ g gelatin, 7.7 g sodium caseinate, 97.0 ml water; $4 - 2.0$ g sodium citrate, 7,7 g sodium caseinate, 97,0 ml water; $5 - 3.0$ g gelatin, 2,0 g sodium citrate 97,0 ml water; $6 - 3.0$ g gelatin, 2,0 g sodium citrate, 7,7 g sodium caseinate, 97,0 ml water; $7 - 3.0$ g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate, 5,0 g sunflower seed kernel concentrate, 97,0 ml water

Investigation of effective viscosity of model solutions of food substances, which are the ingredients of a cheese structured semi-product on the basis of nonfat lactic cheese with the use of sunflower seed kernel concentrate, let qualitatively assess the comparative value of intermolecular interactions and the form of particles in the solutions. All these solutions contain equal amount of water.

The dependence of ln_{*n*} on 1/T for the solution containing sunflower seed kernel concentrate has three straight-line portions that is predetermined by intermolecular interactions of different force. The largest activation energy E is characteristic for the solution of gelatin with sodium caseinate, where, at low

temperatures, there is spatial structure of protein gel created in the result of mixing globular caseinate and fibrillary gelatin. Addition of sodium citrate results in the reduction of activation energy of the solutions. The complex formed due to hydrogen-bonds at the interaction of sodium citrate with proteins makes the molecules of sodium caseinate and gelatin hydrophobial. The energy of intermolecular bonds reduces, particularly at temperature rise. The exception makes the solution containing sunflower seed kernel concentrate. According to the Einstein equilibrium, the dispersed system with the particles containing slush has bigger viscosity than other model solutions, and, respectively, bigger activation energy E_2 of molecular interaction, that is seen from the results of the investigation (table 2.20).

Table 2.20

N_2	Instant gelatin, g	Sodium caseinate, g	Sodium citrate, g	Concentrate of sunflower seed kernel, g	Drinking water, ml
		7,7			97,0
$\overline{2}$	3,0				97,0
3	3,0	7.7			97,0
$\overline{4}$		7,7	2,0		97,0
5	3,0		2,0		97,0
6	3,0	7,7	2,0		97,0
7	3,0	7,7	2,0	5,0	97,0

The composition of standardized test solutions of model system

Fig. 2.26. The dependence of relative viscosity of model solutions on temperature: $1 - 7.7$ g of sodium caseinate, 97,0 ml of water; $2 - 3.0$ g of gelatin, 97,0 ml of water

Effective viscosity of water sufficiently depends on temperature and falls from 1,005 10⁻³ MPa \times s at temperature 20[°] C to 0,3565·10⁻³ MPa \times s at temperature 80° С. The dependences of relative viscosity on temperature for the solutions under research are presented in fig. 2.26…2.32 respectively.

It is found that the process of the dependence of relative viscosity on temperature for the solution of sodium caseinate with sodium citrate differs from other solutions. Growth of this solution's viscosity (curve 1 in fig. 2.26) in the temperatures interval $T=20...40^{\circ}$ C testifies that chemical bonds between sodium citrate and sodium caseinate are not very strong. Sodium citrate anion has three negative charges and is probably connected with positively charged amino-groups of globular sodium caseinate.

Fig.2.27. Dependence of relative viscosity of model solutions on temperature: $3 - 3.0$ g gelatins, 7.7 g sodium caseinate, 97.0 ml water; $4 - 2.0$ r sodium citrate, 7,7 g sodium caseinate, 97,0 ml water; $5 - 3.0$ g gelatin, 2,0 Γ sodium citrate 97,0 ml water; $6 - 3.0$ g gelatin, 2.0 g sodium citrate, 7,7 g sodium caseinate, 97,0 ml water

Figure 2.28 shows that the largest molecular forces possess a solution with the addition of sunflower seed kernels. Protein of the particles of sunflower seeds kernel concentrate interacts with molecules of sodium caseinate and gelatin, and changes the structure as a whole, thus significantly increasing the viscosity.

For all solutions at all temperatures coefficients α are calculated. The dependence α on temperature is shown in Fig. 2.28 ... 2.33.

All curves tend to minimum α , i.e. to aniso-diametral features, that is achieved at 50 ... 60 ° C. Chemical bond formed between sodium citrate and sodium caseinate (curve 3 in Fig. 2.30), increases α . This bond slows down reduction α with temperature.

 Fig.2.28. Dependence of relative viscosity on temperature for model solution: $7 - 3.0$ g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate, 5,0 g sunflower seed kernel concentrate, 97,0 ml water

Fig. 2.29. Dependence of coefficient α in Einstein equation on temperature for model solutions: $1 - 7.7$ g sodium caseinate, 97,0 ml water;

solutions: $2 - 3.0$ g gelatin, 97,0 ml water; $3 - 3.0$ g gelatin, 7,7 g sodium caseinate, 97,0 ml water; $4 - 2.0$ g sodium citrate, 7,7 g sodium caseinate, 97,0 ml water;

Investigations of effective viscosity and activation energy of model solutions of constituents of structured semi-finished cheese depending on the temperature proved that mixing sodium caseinate and gelatin solutions leads to the significant increase in viscosity, but with the temperature decrease below 30 °C a strong fixed spatial gel structure is formed. It is shown that there is slight chemical conjunction between sodium caseinate and sodium citrate. The increase of temperature lowers aniso-diametral features of particles in the solutions of compound substances of a product and investigation of effective viscosity of the solutions allows qualitatively assess intermolecular reciprocity in a cheese structured semi-product.

Fig. 2.31. Dependence of α coefficient in the Einstein equation on the temperature for standardized test solutions: $6 - 3.0$ g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate, 97,0 ml water

Fig. 2.32. Dependence of α coefficient in the Einstein equation on the temperature for standardized test solutions: $5 - 3.0$ g gelatin, 2.0 g sodium citrate; 97,0 ml water; $7 - 3.0$ g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate, 5.0 g sunflower seed concentrate, 97,0 ml water
2.5.2. Investigation of supramolecular structure of standardized test solutions

It is known that at certain concentrations in a solution of proteins, polysaccharides, and such structuring agents as gelatin, agar, furcelaran, etc., create particles, the accumulation of which is called supramolecular structure. The research of the structure will permit to explain the mechanisms of gelformation in these systems.

Special interest gains investigation of supramolecular structure of compound nutritive objects containing different proteins. The elaborated new cheese structured semi-product is one of such products. The proteins differing in a spatial structural organization – namely globular casein and fibrillous gelatin comprise its structure.

The standardized test solutions of the components of a cheese structured semi-product on the basis of fermented fat-free melted cheese with the use of sunflower seed concentrate was chosen for study. Their composition is presented in Table 2.21.

Table 2.21

The composition of standardized test solutions

The results of the calculations of supramolecular particles radius and their concentration in standardized test solutions are presented in Table 2.22. These results demonstrate that during the addition of sodium caseinate to the solution of gelatin the size of particles sharply reduce. It means that molecules of globular sodium caseinate and fibrillous gelatin interact. It results in the formation of spatial strong structure of protein gel in the solutions containing gelatin and sodium caseinate.

Table 2.22

Results of calculating SMPs and their concentration in standardized test solutions

So, the existence of the interaction between the molecules of globular sodium caseinate and fibrillous gelatin in standardized test solutions of nutritive substances is proved. In the solutions containing these components spatial strong structure of protein gel will form during the refrigeration. It is proved that changing the concentration and correlation of sodium caseinate and gelatin it is possible to manage the process of gel-formation in nutritive systems.

2.5.3. Featuring functional-technological properties of gels of standardized test system

Investigation of the kinetics of structure-formation of 3% solution of instant gelatin (Table 2.23) at temperature 20 ± 1 °C showed that after $(25...35)\times60^2$ s the strength of gels remained at the level 345...365 g. according to the graph, the duration of various gels' structure formation ends practically after 25×60^2 s (fig. 2.31).

The kinetics of gel structure-formation in the presence of sodium nitrate and sodium caseinate (fig.2.31, curves 2,3,4) attract special interest. At the starting point of phase transition of liquid-gel during the first 25×60^2 s the strength of gelatin gel with sodium citrate, and gelatin with sodium caseinate sufficiently grows in comparison with pure gelatin (curve 1). Joint addition of sodium citrate and sodium caseinate to gelatin during the same period at the initial stage of structure-formation (curve 4) strengthens gel in a greater degree comparing to the samples (2 and 3).

The composition of standardized test solutions of gel

The increase of the strength of gelatin gel with the addition of sodium citrate occurs in the result of electrostatic interaction between amino groups of macromolecules with anions of salts of organic acids. Such interaction reduces the number of positive charges in the molecules of gelatin and leads to their hydrophobization with corresponding changes in the molecules conformation.

Fig. 2.33. Dependence of the strength of gels of standardized test solutions on the duration of structure-formation: $1 - 3.0$ g gelatin; $2 - 3.0$ g gelatin g gelatin, 2,0 g sodium citrate; $3 - 3.0$ g gelatin, 7,7 g sodium caseinate; $4 - 3.0$ g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate; $5 - 3.0$ g gelatin, 5,0 g sunflower seed kernel concentrate; $6 - 3.0$ g gelatin, 2,0 g sodium citrate, 7,7 g sodium caseinate, 5,0 g sunflower seed kernel concentrate

This results in strengthening intermolecular hydrogen bonds and such change of spirals of collagen plication that results in the increase of the number of transitional zones of gel carcass and growth of its strength.Addition of sodium caseinate to gelatin strengthens the gel system structure due to the interfusion of globular casein and fibrillated gelatin that promotes the creation of their complex and leads to the change of molecular mass.

Table 2.24 presents the results of investigating the gels strength, temperature of structure-formation, melting and difference between them. Standardized test solutions investigated at the temperature of melting the created gels are place in the raw $6>1$, which is similar to the raw of their placement by the strength of gels creation, by the viscosity of the solutions creation and temperature of structure-formation.

The temperature of structure-formation and melting increases at the addition of the ingredients (sodium citrate, sodium caseinate, sunflower seed kernel concentrate) to gelatin increases, the difference between these temperatures $(t_{\text{mel}}-t_{\text{str}})$ decreases. It may be connected with close location of structural elements of gel during their creation and melting [8, 9]. Besides, addition of the ingredients to gelatin can decrease the energy of activating formation of supramolecular structures.

Decrease of the temperature $(t_{mel}-t_{str})$ is stipulated by the presence of double molecular spirals as a main bundle of gels net in standardized test solutions containing sodium caseinate, sodium citrate and sunflower seed kernel concentrate.

Table 2.24

Nº of standardized test solution	Strength of solutions gel, g	Gel's structure- standardized test formation temperature, $\mathfrak{t}_{\rm str}$ °C	Gel's melting temperature, $t_{\rm mel}$ °C	$t_{\text{mel}}-t_{\text{str}}$ $^{\circ}C$
	345 ± 16	$19,0,\pm 0,2$	33.0 ± 0.3	$14,0\pm0,5$
	371 ± 14	$21,5 \pm 0.3$	34.5 ± 0.3	$13,0\pm0,5$
	401 ± 15	$24,0, \pm 0,2$	$35,0, \pm 0.2$	$11,0\pm0.4$
	427 ± 16	$25,0,\pm 0,3$	36.0 ± 0.4	$10,0 \pm 0,7$
	441 ± 17	$28,5 \pm 0.4$	$36,5 \pm 0,4$	$8,0\pm0,8$
	597 ± 18	30.0 ± 0.5	37.0 ± 0.5	7.0 ± 0.7

The indexes of strength, structure-formation temperature, melting of gel of standardized test solutions

Increase of strength, temperature of structure-formation and melting in the presence of the ingredients can be explained by the change of hydrogen bonds [50], because the factors changing the net of hydrogen bonds are primarily the decrease of the temperature of structure-formation and melting during the addition of the salts of organic acids, spirits, different jellies, etc. [156].

The investigations of gels of standardized test systems of a cheese structured semi-product based on lactic melted cheese prove that the content of the ingredients: sodium citrate, sodium caseinate and sunflower seed kernel concentrate increase thermal stability (fig. 2.34).

It is established that at temperature 30° C 3,0% gelatin gel's thermal stability grows to 480 ± 21 c 480 ± 21 c. Thermal stability grows to 720 ± 34 c at the addition of sodium caseinate.

Fig. 2.34. Dependence of the duration of thermal stability of gels of standardized test solutions on temperature: $1 - 3.0$ g gelatin, 97,0 ml water; $2 - 3.0$ g gelatin, 2,0 g sodium citrate $97,0$ ml water; $3 - 3,0$ g gelatin, 7,7 g sodium caseinate, 97.0 ml water; $4 - 3.0$ g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate, 97.0 ml water; $5 - 3.0$ g gelatin, 5.0 g sunflower seed kernel concentrate, 97,0 ml water; $6 - 3.0$ r g gelatin, 2.0 g sodium citrate, 7.7 g sodium caseinate, 5,0 g sunflower seed kernel concentrate, 97,0 ml water

It is worth noting that the investigated gels are placed according to their thermal stability in the raw $6 > 5 > 4 > 3 > 2 > 1$. The same regularity is similar for the raw by the strength, temperature of structure-formation and melting.

Also the strength of interphase adsorption layers of standardized test solutions, to which belong the nutrients of a cheese structured semi-product on the basis of lactic non-fat defrosted cheese, was researched.

The composition of standardized test solutions chosen for the research of strength between interphase adsorption layers on the basis of sodium caseinate is presented in Table 2.25.

Table 2.25

The composition of standardized test solutions based on sodium caseinate

Results of the calculations of boundary traction of interphase adsorption layers' shift are presented in Table 2.26.

Тable 2.26

Results of the investigations of breaking point of interphase adsorption layers' shift of sample models

Calculations of breaking point of interphase adsorption layers' shift for the solutions under research showed that the strongest interphase adsorption layer is formed for the solution №5, which contains sodium caseinate solution, gelatin, sodium citrate and sunflower seed kernel concentrate. This is stipulated by the creation of strong protein complex among sunflower seed kernel concentrate, sodium caseinate and gelatin. Addition of sodium citrate diminishes the strength of interphase adsorption layer, but addition of gelatin helps to form stronger adsorption layer.

Investigation of the kinetics of structure formation for 3,0% solution of instant gelatin at 20 ± 1 °C showed that after (25 ... 35) × 60 × 60 sec the strength of

gels remains at the level 345...365 g. Addition of sodium citrate, sodium caseinate, sunflower seeds kernel concentrate increases the strength of the structure. These additives increase the structure and melting temperature, but reduce difference between them. The content of the ingredients increases thermal stability of gels of model systems. The presence of gelatin, sodium citrate and sunflower seeds kernel concentrate increases breaking point shift between phase adsorption layers.

2.5.4. Study of evaporation heat and energy links of moisture in model solutions gels

Evaporation heat of model solutions' gels calculated by thermographic data is presented in table 2.27.

Таble 2.27

The influence of additives on changes of heat of water evaporation in gels of standardized test solutions

The received data confirm that all the additives included in the gels under research, regardless of their nature, increase the heat of water evaporation. At low temperatures, when the system is in a structured state, heat of vaporization is higher. This indicates that the moisture in the gels is more tightly bound than at high temperatures when the system is in a molten state. Depending on the type of additive, heat of gels vaporization in model solutions at the temperature to 30°C is higher than the temperature above 70°C, and ranges from 2.13 to 31.41 kJ/mol. This is especially noticeable when sodium caseinate and sunflower seeds kernel concentrate are added to gels of model solutions.

Table 2.27 shows that the ingredients added to gelatin increase energy of water molecules and the compresence in the systems under research, sodium citrate, sodium caseinate and sunflower seeds kernel concentrate increase significantly.

We calculated the energy of water molecules, results of the calculation are presented in Table 2.28.

Table 2.28

Content of gels of standardized test solutions	Cohesive energy of water molecules, KJ/mol	
	to 30° C	after 70° C
$3,0$ g gelatin, 97,0 ml water	42,13	35,47
3,0 g gelatin, 7,7 g sodium caseinate, 97,0 ml water	45,06	41,74
3.0 g gelatin, 2.0 g sodium citrate, 97.0 ml water	48,83	43,19
3.0 g gelatin, 7.7 g sodium caseinate, 2.0 g sodium citrate, 97,0 ml water	62,15	44,38
3,0 g gelatin, 7,7 g sodium caseinate, 2,0 g sodium citrate, 5,0 g sunflower seed kernek concentrate, 97,0 ml water	84,36	46,57

The impact of additives on the change of cohesive energy of water molecules in gels of standardized test solutions

As noted in previous sections, compatible presence of sodium citrate, sodium caseinate and especially of sunflower seeds kernel concentrate greatly increases functional and technological properties (strength, speed, structure forming, melting point and gelation, thermal stability). Comparison of heat evaporation and cohesive energy of water with the above mentioned parameters allows to correlate the method. Heat of water vaporization and cohesive energy increased with the growth rate of structure, melting temperature, gelation and heat resistance.

2.5.5. Determination of the forms of the cohesion of the moisture of gels of model solutions by the method of thermograms of differentialscanning calorimetry (DSC)

Taking into account the fact that semi-finished structured cheese is a complex heterogeneous system, referring to products with high moisture content, binding of which is a characteristic feature of the product. The influence of main ingredients (Fig. 2.35-2.37) on binding water and duration of gelation in model systems of a structured semi-product that occur during heating and cooling are studied experimentally, and temperature ranges of phase transitions are determined.

The variation of DSC signal in the first sample containing gelatin (Fig. 2.35) shows irreversible process that occurs when cycling. The first characteristic exothermic heating process is observed at temperatures of 30 ... 45°C, indicating the formation of primary hydration structure and binding of moisture. Thus water molecules are arranged between the elements of supramolecular structures, increasing the amount of polymer (swelling). However, further increase in temperature to 45 ... 50°C endothermic transition associated with the deployment of macromolecules is observed. The rate of swelling decreases rapidly, as evidenced by the absence of thermal effects at $t = 55...65$ ^o C

Fig. 2.35. DSC curves of heating-cooling of modeling solution gel containing gelatin 3.0%

With further heating at temperatures of 70...90° C exothermic transition is again observed. This phenomenon is probably caused by the second internal structural stage of swelling the system, when, with the increasing diffusivity, water molecules begin to penetrate inside macromolecules, forming new internal structural connections.

The process of swelling the system continues for the next three stages of thermal cycling. This assessment is confirmed by the value of thermal effect carried out before. This forms a stable dispersed structure in which, with temperature decrease, intermolecular complexes start forming as a result of reducing mobility of solvent molecules, as evidenced by exothermic processes in the temperature range 30 ... 40° C = (20, 30, 43) \times 60 s.

Fig. 2.36. DSC curves of heating-cooling of modeling solution gel containing 3.0% gelatin and sodium caseinate 7.7%

Thus for all experiments the amount of heat in the range of 20 \dots 90 ° C (total for all cycles) in relative units (the amount of heat transferred in the first cycle was taken as 100%) was calculated. For the first sample Oef = -133% it means that the amount of heat abstracted by cooling the sample to 133% greater than the amount of heat fed when heated. This testifies to the irreversibility of the process, during which the heat released swelling (structuring) system.

For the second sample containing gelatin and sodium caseinate (fig.2.36), irreversible process of structuring that occurs is also a characteristic feature, but it is much smaller than the first - the value Qef = -82%. Probably it happens in the result of more intensive structuring of model system and reduction of the mobility of water molecules.

The third and the fourth cycles of thermal cycling are practically symmetric. It allows us think the process of structuring up to 45 min. is coming to its end. The other specificity is the fact that during the first cycle with temperature increase from 30 до 80° С endothermic process of macromolecules expanding takes place, but not the process of water molecules hydration by supramolecular structure. Structuring starts at temperature t>85° С, molecules of water actively defund inside macromolecules forming new intra-structural links. The following heating and refrigeration (cycles 3, 4) practically do not change disperse properties of the system.

Fig. 2.37. DSC-curves of heating-cooling of the gel of a model solution with 3,0% gelatin and 5% sunflower seed kernel concentrate So, it is possible to consider that the duration of structuring for this sample equals the first stage duration – 10×60 s.

The third sample (fig.2.37) sufficiently differs from the two previous samples. First, practical reversibility of thermal cycling is well seen (symmetric view of DSC signal during thermal cycling). Calculations of $Q_{\text{ed}} = 16\%$,

(effective thermal effect close to zero) prove this. Secondly, Q_{ed} is positive, i.e. the received amount of heat to the sample is bigger than the one given in the process of cooling. It means that the process of heat destruction in a model system prevails. If exothermic is characteristic for the first cycle (i.e. the process of model system's gelling at $t = 30...40^{\circ}$ C), for the second cycle endothermic process of the structure destruction occurs at t=95…85 °С.

Therefore, rational amount of the ingredients in a cheese structured semi-product – gelatin 3%, defrosted nonfat lactic cheese 50,0 %, sunflower seed kernel concentrate 5%.

2.5.6. Investigating IR-spectrums of dried films of the gel of standardized test solutions

With the account of receipt composition of cheese structured semiproduct on the basis of defrosted nonfat lactic cheese with the use of sunflower seed kernel concentrate the authors prepared the samples of jellied gelatin, the composition of which is presented in Table 2.29.

Table 2.29

N ₂	Instant gelatin, g	Sodium caseinate,	Sodium citrate, g	Sunflower seed kernel concentrate, g	Drinking water, ml
	3,0				97,0
\overline{c}	3,0				97,0
	3,0		2,0		97.0
	3,0			5,0	97.0
	3,0				
n	3,0				

Composition of the samples of dried films of standardized test solutions

Figures 2.38-2.43 present IR-spectrum of dried films of jellied gelatin. We can see there a wide line characteristic for all proteins at 3300 cm^{-1} . It is stipulated by valence vibrations of the link $N-H$ in $-NH₂$ groups, which participate in the creation of hydrogenous links and valence vibrations of links in O-H groups at $3400-3200$ cm⁻¹. He absorption bands $3100-3050$ cm and 1650-1600 сm correspond valence and deformation vibrations of N-H link in NH_3^+ groups. Absorption peaks 1350-1300 cm⁻¹ are connected with valence vibrations of C-N link. The lines within $1480-1430$ cm⁻¹ are predetermined by deformation vibrations of symmetrical links CH₂. The absorption within the range $1250-1220$ cm⁻¹ can be connected with deformation vibration of C-H links. The absorption bands within 1150-1075 cm^{-1} and 1210-1100 cm^{-1} are predetermined by valence vibrations of C-O links in СН–ОН and С–ОН groups, which belong to secondary and tertiary alcohols.

Fig. 2.38. ІR- spectrum of dried film of the gel of standardized test solution of gelatin

IR-spectra of dried films of jellied gelatin with the addition of the components of a cheese structured semi-product (samples 2-6, table 2.29) were registered according to the dried film of gelatin (sample №1), and presented in fig. 2.36…2.41.

Fig. 2.39. ІR- spectrum of dried film of the gel of standardized test solution of gelatin with sodium citrate

The comparison of these two spectra show that each has two areas of peaks within $3460-3142$ cm⁻¹ and $1700-1516$ cm⁻¹. The number of peaks in these areas, absorption intensity and wave numbers of peaks for each of the samples differ. Table 3.30 presents characteristics of peaks with IR-spectra of the samples under research.

Fig. 2.40 IR-spectrum of a dried film of the gel of standardized test solution of gelatin with sunflower seed kernel concentrate

Fig. 2.41. IR-spectrum of a dried film of the gel of standardized test solution of gelatin with sodium caseinate and sodium citrate

The results of investigating IR-spectra of the jellied gelatin with the addition of the components of a cheese structured semi-product demonstrate that the area $3460-3142$ cm⁻¹ corresponds valence vibrations – OH and valence vibrations of N-H link in $NH₂$ groups, which participate in the formation of hydrogenous links. Intensity of these absorption lines increases in the samples 2, 5, 6, 3, 4.

Widening of the area 3332-3141 cm⁻¹ for sample \mathcal{N}_2 3 states about the redistribution of hydrogenous links. Reduction of the area towards larger frequency vibrations means that intermolecular links for the samples 4, 5, 6 increase.

The area of absorption peaks $1700-1600$ cm⁻¹ corresponds deformation vibrations N-H and shifts to larger vibration frequencies for all investigated samples which means that intermolecular links increase. Trace slip of the band towards high frequency area for the samples №№ 3-6 is the same, but for sample \mathcal{N} 2 it is 13-15 cm⁻¹ longer. The samples are located in the line of samples \mathcal{N} <u>o</u> 2, 5, 4, 3, 6 according to the intensity of absorption peaks in this area.

The area 1560-1500 cm⁻¹ corresponds the deformation of COO non-flat vibrations in the result of dissociating carboxylic group in water solutions. Strong peaks of absorption in this area are characteristic for the samples $N_{\text{e}}N_{\text{e}}$ 2, 4, 5. For the sample № 6 the absorption peaks, which correspond N-H deformation vibrations, are so strong that the contribution of vibrations of COOgroups is not sufficient.

Fig. 2.42. IR-spectrum of a dried film of the gel of standardized test solution of gelatin with sodium caseinate and sunflower seed kernel concentrate

For all samples except the third one, characteristic is an increase of intermolecular bonds, which is evidenced by a significant shift of the region of stretching vibration groups - OH toward higher frequencies.

Therefore, in the result of IR-spectra analysis of dried films of jellied gelatin with the addition of the components of a cheese structured semi-product the investigated samples can be placed in a line N_2N_2 3, 2, 5, 4, 6 by the strength of the created structure.

Table 2.30

Areas of peaks, cm^{-1}	Strong peaks, cm ⁻¹	Absorption intensity., $\frac{0}{0}$	Bands assignment	Conclusions		
1	\mathfrak{D}	3	4	5		
Sample No 2						
3339-3271	3338,56 3202,50 3271,77	80 110 130	Valence vibrations- OH; valence vibrations of N-Hlinkin $NH2$ groups	The largest peaks correspond valence OH vibrations		
1700-1534	1564,60 1546,05 1534,18	600 1180 1600	$N-H$ deformatio n vibrations in NH_3 ⁺ groups and COO ² deformatio n vibrations	The area is extended towards large vibration frequencies, which means the increase of intermolecular links. The biggest peaks correspond COO deformation vibrations		
			Sample N_2 3			
3332-3141	3316,75 3297,47 3141,39	400 400 400	$\overline{\text{Valence}}$ vibrations - OH; N-H link valence vibrations in $NH2$ groups	Extension of the area speaks for the redistribution of hydrogenous links. Peaks 3316,75 and 3141,39 correspond OH valence vibrations.		
1685-1534	1684,78 1661,20 1534,01	8200 400 2500	$N-H$ deformatio n vibrations in NH_3 ⁺ groups and COO ² deformatio n vibrations	The area is extended towards large vibration frequencies that speak for the increase of intermolecular links. Peaks 1684,78 and 1661,20 correspond N-H deformation vibrations.		

Results of investigating IR-spectrum of dried films of the gel of standardized test solutions

Table 2.30 continued

2.5.7. Investigating protein-fractional composition of standardized test solutions

The proteins of sunflower seed kernel concentrate, caseinate and gelatin are the components of a new product. Their standardized test solutions (table 2.31) were prepared for the investigation of fractional protein composition.

Table 2.31

 $1 \quad - \quad 3,0 \quad 1 \quad - \quad 97,0$ $2 \mid 7,7 \mid$ - \mid 97,0 $3 \mid - \mid$ - \mid 5,0 \mid 97,0 4 7,7 3,0 1 - 97,0 5 - 3,0 5,0 97,0 6 7,7 - 5,0 97,0 7 7,7 3,0 5,0 97,0

Instant gelatin, g

N₀ N_o

Sodium caseinate, g

Мм=80,41 (23,96%), Мм= 55,68 (6,59%), Мм=43,08 (24,45%), $M_M=35.96$ (41,81%). In the figures 2.43-2.50 the results of electrophoretic division of proteins of various fractions of standardized test solutions by the molecular masses are presented.

The analysis of main fractions of proteins received in the result of electrophoretic division of the investigated samples, and comparison of Mm fractions, the abundance ration of which related to the total amount of protein is the biggest, showed that main fractions have Mm=80,41 (23,96%), Mm = 55,68 (6,59%), Mm =43,08 (24,45%), Mm=35,96 (41,81%) for the sample containing only gelatin (fig. 2.43), and which is the α -particles of collagen.

Fig 2.44 - Molecular-weight distribution of proteins of the standardized test solution of gelatin

Fig. 2.43 Electrophoretic division of proteins of various fractions by the molecular masses in SDS-PAAG 12,5% of standardized test solutions: $1 -$ gelatin; 2 sodium caseinate; 3 – sunflower seeds kernel proteins; 4 – gelatin and sodium caseinate; 5 – gelatin and sunflower seeds kernel proteins; $6 -$
sodium caseinate and caseinate and sunflower seeds kernel proteins; 7 – gelatin,
sodium caseinate and caseinate and sunflower seeds kernel proteins; 8 – standard.

For the standardized test solution of sunflower seed kernel concentrate (fig. 2.45) - Mm=69.52 (0.88%), Mm =67.78 (1.15%), Mm =64.03 (1.63%), Mm =60,92 (5,8%), Mm =59,91 (1,28%), Mm =54,40 (9,75%), Mm =49,47 $(4,51\%)$, Mm =45,30 $(3,21\%)$, Mm =43,47 $(10,1\%)$, Mm =38,60 $(0,62\%)$, Mm $=$ 32,57 (7,63%), Mm $=$ 30,00 (12,33%), Mm $=$ 25,01 (14,35%), Mm $=$ 9.07 $(15,57\%)$.

Fig 2.45 – Molecular-weight distribution of proteins of the standardized test solution of sodium caseinate

New fractions Mm=52,26 (34,44%), Mm =38,32 (23,12%) and Mm $=33,56$ $(1,27\%)$ appear in the result of electrophoretic division of the standardized test solution of gelatin and sodium caseinate (fig. 2.47) in comparison with fractional composition of gelatin (fig. 2.44) and sodium caseinate (fig. 2.45).

Fig 2.46 – Molecular-weight distribution of proteins of the standardized test solution of sunflower seed kernel concentrate

Fig 2.47 – Molecular-weight distribution of proteins of the standardized test solution of gelatin and sodium caseinate

test solution of sodium caseinate and sunflower seed kernel concentrate Fig 2.48 – Molecular-weight distribution of proteins of the standardized

Five new fractions appear for the standardized test solution of gelatin and sunflower seed kernel concentrate in comparison with the composition of gelatin (fig. 2.44) and sunflower seed kernel concentrate (fig. 2.46). The fractions that were present in the sample of sunflower seed kernel concentrate with Mm=49,47 (4.51%) , Mm =38,60 (0.62%) , Mm =30,00 (12.33%) , Mm =9,07 (15.57%) are absent for the sample $N₂$ 5.

This fact speaks for the interaction of the proteins of gelatin and sunflower seed kernel concentrate. Molecular masses of new fractions are higher in comparison with Mm fractions of proteins of sunflower seed kernel concentrate.

New fractions with Mm=55,10 (4,61%), Mm=50,94 (11,64%), Мm=33,70 (2,09%) appear in the result of electrophoretic division of the standardized test solution of sodium caseinate and sunflower seed concentrate (fig. 2.49) in comparison with the fraction composition of sodium caseinate (fig. 2.45) and sunflower seed kernel concentrate. Protein fractions of sodium caseinate with Мm=54,28 (24,77%) and sunflower seed kernel concentrate with Мм=54,40 (9,75%), Мм=49,47 (4,51%) and Мм=45,30 (3,21%) are absent (fig. 2.49). reduction of fractions with large Mm and creation of protein complex with smaller Mm can be stipulated by the break of sodium caseinate circuits under the influence of the proteins of sunflower seed kernel concentrate.

Fig 2.49 – Molecular-weight distribution of proteins of the standardized test solution of gelatin, sodium caseinate and sunflower seed kernel concentrate

New ten protein fractions, Mm of which are higher than protein fractions of the investigated samples of gelatin, sodium caseinate and sunflower seed kernel concentrate (fig. 2.44-2.50) appear for the standardized test solution of gelatin, sodium caseinate and sunflower seed kernel concentrate (fig. 2.50). It proves the formation of the links between the proteins of sunflower seed kernel concentrate, gelatin and sodium caseinate.

Quality analysis of the received results of electrophoretic division of proteins of various fractions by the molecular masses of the investigated

samples showed that between the proteins of sodium caseinate and α-particles of collagen of gelatin the links are created. The proteins of sunflower seed kernel concentrate also interact with α-particles of collagen with the formation of molecules with bigger Mm. Some links are also formed between the proteins of sodium caseinate and sunflower seed kernel concentrate. Nevertheless, some circuits of sodium caseinate break, that results in in the creation of proteins with smaller Mm. The formed links are not covalent but may have electrostatic nature.

Fig 2.50 –Molecular-weight distribution of proteins of the standardized test solution of sodium caseinate and sunflower seed kernel concentrate

CHAPTER 3

DEVELOPMENT OF TECHNOLOGY OF A CHEESE STRUCTURED SEMI-PRODUCT BASED ON REFRIGERATED NONFAT LACTIC CHEESE WITH THR USE OF SUNFLOWER SEED KERNEL CONCENTRATE

3.1. Development of the recipe and technology of a cheese structured semi-product

The complex of experimental investigations with main ingredients, an innovative technology model (fig. 2.1), a model of technological scheme (fig. 2.2) and ready product allowed to substantiate the recipe scientifically (table 3.1), which is enshrined in the developed technological conditions TC, and the structure of the technological process system (table 3.2), and the scheme of technological process (fig. 3.1) of a cheese structured semi-product based on the refrigerated nonfat lactic cheese with the use of sunflower seed kernel concentrate, which is normatively fixed in the developed technological instruction.

Most of the elaborations of technological process of manufacturing a cheese structured semi-product based on milk and plant protein raw material were systematized, according to which a technological scheme can be divided to several subsystems, whose functioning will result in the appearance of a new product.

The peculiarity of the technological process of manufacturing a structured cheese product is the use of defrosted nonfat lactic cheese, transition of milk protein to liquid form, participation in its formation, stabilization of the emulsion, and use of sunflower seed kernel concentrate during the stabilization of emulsive system in the process of thermal treatment within $80\pm2^{\circ}$ C and its structuration.

The realization of functional properties of milk proteins of gelatin and sunflower seed kernel concentrate results, according to working hypothesis, in the increase of effective viscosity, boundary traction of the shift of interphase adsorption layers, energy of the links of water molecules, and reduction of the structuration. This supports the process of the stabilization of emulsion and emulsive system.

The complex of investigations allowed scientifically substantiate the composition (table 3.1) and technology of the cheese structured semi-product based on milk and plant raw material.

Technological system of manufacturing cheese structured semi-product based on milk and plant raw material consists of the following subsystems (fig. 3.1): $D -$ "Creation of dispersed medium": $C -$ "Formation of the emulsion": $B -$ "Formation and stabilization of emulsive system, thermal treatment"; A – "Creation of a cheesestructured seni-productt".

Table 3.1

Raw material	Weigh fraction of dry substances, %	Aggregate expenditures of raw material with the account of losses during the technological process		
		naturally, kg	In dry substances, $\frac{0}{0}$	
Defrosted				
nonfat lactic	21,19	51,40	10,89	
cheese				
Purified oil	99,90	15,41	15,39	
Edible	89,10	15,41	13,73	
vegetable oil				
Sunflower seed				
kernel	93,40	5,14	4,80	
concentrate				
Instant gelatin	88,30	3,08	2,72	
Sodium citrate	96,00	2,06	1,98	
«Extra» salt	96,50	1,03	0,99	
Potassium	95,00	0,10	0,10	
sorbate*				
Drinking water		9,17		
Total		102,80	50,60	
Output		100,00	49,22	

The consolidated recipe of the cheese structured semi-product per 100 kg

* It is used for the durable product

It is worth saying that functioning of the system in general is ensured by the functioning of some components according to the purpose defined (table 3.2).

D subsystem – "Formation of protein background". At this stage instant gelatin is introduced to the defrosted nonfat lactic cheese at temperature of $35\pm2^{\circ}$ C with mixing it at $\omega=25\pm2^{\circ}$ for $(3\pm1)\times60$ s, and milk protein is transformed to liquid state by adding the solution of sodium citrate under condition of constant mixing for $(30\pm3)\times60$ s. At the same time complex formation of proteins starts that results in a slight increase of viscosity and creation of dispersed medium.

C subsystem – "Formation of emulsion". At this stage the purified deodorized sunflower oil and melted edible vegetable oil emulsify to dispersed medium (the complex - protein of the defrosted nonfat lactic cheese transferred to soluble state, and the solution of gelatin due to the movement of free moisture of lactic cheese) at temperature of $35\pm2^{\circ}$ C for $(8\pm1)\times60s$ and mixing machine rotation speed $50 \pm 2c^{-1}$.

Table 3.2

The structure of technological system and the purpose of the components' functioning

B subsystem – "Thermal treatment, complex formation and stabilization of emulsive system". After the emulsification of oil and melted edible vegetable oil during its intensive mixing, the sunflower seed kernel concentrate is introduced. After thermal treatment at temperature of $80\pm2\degree$ C for $(8\pm2)\times60$ s the viscosity of disperse emulsive system and the speed of structure formation of a ready product grow. For the provision of long term of storage, the solution of potassium sorbate is introduced to the emulsive system.

A subsystem – "Creation of a cheese structured semi-product". For the fulfilment of the tasks of the subsystem, after thermal treatment, the flowing product was packed in a consumer tare, where final structure formation occurred. It was cooled to the temperature of $4\pm 2^{\circ}$ C. The chilled prepackaged product can be stored at such temperatue for 28 days.

Fig. 3.1. Technological scheme of manufacturing cheese structured semiproduct with the use of sunflower seed kernel concentrate: $\sum \sum$ [] operations carried out only for the manufacture of a durable cheese structured semi-product

3.2 Investigation of structural-mechanical characteristics of a cheese structured semi-product during storage

Storage is one of important stages influencing the quality of ready products. It stipulates the necessity of investigating the influence of the regimes and terms of storage on quality parameters of a cheese structured semi-product.

The changes of structural-mechanical characteristics of a packed fresh cheese structured semi-product are studied for the determination of rational duration of storage at temperature of $+4\pm2^{\circ}$ C for 35 days (fig. 3.22). At the same time the reversible, irreversible, common deformation, tension, compliance, conditionally momentary module, plastic and elastic viscosity are specified (table 3.3) [66, 75, 157, 209].

It should be noted that storage conditions for the cheese structured semi-product based on nonfat lactic cheese were chosen with the account of the requirements to the storage of this type of products.

Fig. 3.2. Kinetics of creeping of the cheese structured semi-product during its storage, days: $1 - 1$; $2 - 7$; $3 - 14$; $4 - 21$; $5 - 28$; $6 - 35$

The analysis of creep curves of the cheese structured semi-product showed that the most yielding is the sample after the first day of storage with common deformation $6032.0 \cdot 10^{-3}$. After seven days of storage common deformation (table 3.3) reduces insufficiently, and equals $5789.0 \cdot 10^{-3}$ that is proved by the slight increase of conditionally momentary module of elasticity to 85,9 Pa. During further storage of the structured cheese product general deformation reduces gradually, in an average 1,2 times every 7 days, and on the 28-th day it equals $3250,0.10^{-3}$.

So, it is possible to think that during the term of storage the compression of the semi-product takes place in the result of partial loss of free

moisture. It is proved by the insufficient growth of conditionally momentary elasticity module and slow growth of highly elastic module.

Table 3.3

Characteristics of the dependence of the parameters of a cheese structured
semi-product on the storage duration

The results of calculations of relative plasticity and elasticity of the cheese structured semi-product (fig. 3.3) prove that during the storage of the ready product to 28 days, its plastic and elastic properties maintain at the same level. But during the further 7 days storage plastic properties reduce at $8\pm1\%$, but elastic properties grow at 20%, that results in a sufficient compression of the structure.

Fig. 3.3. The dependence of relative plasticity – 1 (Pl), elasticity – 2 (El), springiness – 3 (Sp) on the duration of the structured semi-product storage

Elasticity of the product doesn't practically change for 28 days, for the next 7 days it gradually grows at $2\pm 0.5\%$. It means that at the 35-th day of the storage it grows only at 6% and doesn't sufficiently influence organoleptic qualities.

3.3. Investigation of nutritive and biological value of a cheese structured semi-product

Nutritive value of foodstuff is determined by the content of proteins, fats, carbohydrates, vitamins and minerals.

Biological and nutritive value of proteins is an integral index that is determined by the quality and number of proteins in a human diet, digestibility of protein by proteinases of the intestinal tract, deimbibition of amino acids, which absorbed to "plastic" needs of the organism [107, 126, 127, 169, 217].

The proteins of nonfat lactic cheese possess a high biological value determined both by the amino acid composition and their digestibility and metabolic transformation of absorbed exogenous amino acids.

The basis of the cheese structured semi-product is defrosted nonfat lactic cheese, in which casein is the main protein. It is known that casein has some specific features assisting it to adapt to the process of digestion [66, 67]. The ability to create clots in acidic medium under the influence of some prosthetic appliances, and in the presence of calcium ions. Casein is well hydrolyzed by the proteolytic enzymes. It allowed the scientists to compare this protein with globular proteins in denaturated state by the hydrolytic ability [138, 222, 227, 232]. Casein refers to the proteins, which form soluble complex aggregates – micella. At the same time it differs from globular proteins by some physical-chemical features and chemical composition.

General chemical indices (table 3.4) and nutritive value (table 3.5) of the cheese structured semi-product on the basis of the defrosted nonfat lactic cheese in the process of storage was determined by the general amount of proteins, fats, vitamins, minerals in it.

Table 3.4

Characteristics of chemical parameters of a structured cheese product during storage, %

Table 3.5

Name of the parameter	Coefficient of the validity of the parameter	Evaluation of organoleptic parameters for storage duration, days		
			28	
Appearance	0,20	4,95	4,95	
Color	0,05	4,88	4,65	
Flavor	0,10	4,85	4,60	
Aroma	0,05	4,84	4,75	
Consistence	0,60	4,96	4,85	
Overall estimation		4,896	4,860	

Organoleptic parameters of a cheese structured semi-product

Analysis of chemical parameters showed that $14,9\pm0,7\%$ of protein substances providing it with main protein-containing ingredients – defrosted nonfat lactic cheese, sunflower seed kernel concentrate and gelatin.

Storage is one of the stages influencing the quality of a ready product, that stipulates the necessity of investigating the influence of the regimes and terms of storage of the product on its quality parameters.

The product was stored at temperature from $+2$ to $+6^{\circ}$ C for 28 days. It should be noted that storage conditions were chosen with the account of the requirements to the storage of the named group of products. The samples were stored in market containers – hermetically packed in plastic glasses. The samples of the cheese structured semi-product with organoleptic, physical-chemical, microbiological parameters fixed in the first day of preparation were used for control.

As table 3.4 shows, the parameters of the cheese structured semiproduct do not change sufficiently in the process of storage. General amount of proteins reduce at 0,7%. It happens due to partial slight hydrolysis of proteins with the formation of free amino acids. That is why it is necessary to study the change of amino acid composition of proteins in a product after the storage for 28 day by the chosen parameters (table 3.6).

Study of organoleptic parameters on the first and the twenty-eighth day of storage (table 3.5) showed that the flavor is slightly fading, the consistence is constraining, the smell is lost.

During the investigations 18 amino acids are identified and quantitatively specified, with the total content of essential amino acids 37,5% that allows to characterize the cheese structured semi-product as a product of high biological value. It is also determined that the number of essential amino acids during storage declined 0,82%, herewith the decline is the most characteristic for phenylalanine -2.9% , tryptophan -2.8% , the parameters of other essential amino acids reduce within 0,4…1,0%. The content of nonessential amino acids falls within 0,3%.

Table 3.6

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Biological value of the cheese structured semi-product by its amino acid composition was assessed through the comparison with amino acid composition of the sample protein FAO/WHO calculating its amino acid composition (table 3.7).

Amino acid score of proteins of a cheese structured semi-product during storage

Both the presence of all essential amino acids and their balanced state is an important parameter of a biologically complete protein. The authors elaborated "threonine" index (table 3.8) for the evaluation of the levels of threonine and tryptophan as a component of the protein of the cheese structured semi-product.

Table 3.8

Table 3.7

Based on the above data we can say that the conditions and duration of storage do not sufficiently influence biological value of the cheese structured semi-product.

In order to determine dynamics of hydrolytic and oxidative transformations in the lipids of the cheese structured semi-product, acid and peroxide numbers (table 3.9).

Table 3.9

The change of acid and peroxide numbers if lipids in a cheese structured semiproduct during storage

In the process of storage the products of triglycerides hydrolysis accumulate that is characterized by a slow covering with a number of free fatty acids (table 3.10)

Table 3.10

The change of acid composition of lipids of a cheese structured semi-product during storage (% from the total amount)

Analysis of the data showed that during storage the amount of unsaturated fatty acids fall: oleinic -5,5%, linoleic -8,2%. Total amount of saturated acids is $43,28\%$, after storage it equals $47,29\%$; unsaturated $-49,62\%$, after storage – 45,59%. Therefore, total amount of unsaturated fatty acids falls at 4,01% due to the increase of the part of saturated acids and unidentified fatty acids. But despite some changes in fatty acidic composition of lipids during storage, fatty component is characterized by a high nutritive and biological value.

The study of vitamin composition showed that a cheese structured semiproduct is rich in fat-soluble vitamin E – tocopherol and water-soluble P-P – niacin.

Analysis of the data during the storage of a cheese structured semiproduct established that the amount of fat-soluble vitamins decline – vitamins A and E 12,1% and 4,1% respectively. At this, the reduction of vitamin C during storage equals 29,1% (table 3.11).

Table 3.11

The change of vitamin content of a cheese structured semi-product, mg/100 g

Analysis of mineral composition of a cheese structured semi-product showed that the contents of potassium (5733 \pm 286 mcg/g) and calcium (495,6 \pm 24,7 mcg/g) are the largest in comparison with the other elements. The content of important elements like plumbum, copper, chromium, nickel and others do not exceed permissible rates (table 3.12).

During the storage, the parameters of some elements changed within the range of the permissible error. So, it is possible to suppose that the value of their losses does not fall outside the limits of the error.

Microbiological and toxicological investigations of a cheese structured semi-product showed that coliform bacterium during storage were steadily absent; pathogenic microorganisms, in particular, *Salmonella*, *Staphylococcus aurеus*, *Listeria monocitogenes* were not found (table 3.13).

For the determination of the term of storage it is important to study microbiological parameters of a cheese structured semi-product (table 3.13). The conducted investigations proved that microbiological parameters conform with the standards of MBR and SN_№ 5061

Table 3.12

The change of mineral composition of a cheese structured semi-product during storage, mcg/g

Table 3.13

The results of toxicological examinations (table 3.14) of a cheese structured semi-product correspond the safety criteria concerning the amount of toxic elements much less than МBR and СН№ 5061 standard requirements to this product [152, 183-189].

Table 3.14

Maximum permissible level of toxic elements, mg/kg

Analysis of experimental data shows that microbiological parameters of a cheese structured semi-product are within the range of the permissible values, regulated by normative documents.

Therefore, after the study of changes of the main nutritive substances and microbiological parameters during the storage, it is possible to say that the cheese structured semi-product is characterized by steady quality parameters during the term of storage.

3.4. Investigation of sensor quality parameters of a cheese structured semi-product

A number of the experiments were carried out for the determination of main organoleptic parameters of a cheese structured semi-product based on lactic cheese. They were directed to the elaboration of numerical scale for sensor evaluation of the ready product by 5-grade system (table 3.15) [43, 47, 63, 81, 180, 205, 206].

The authors carried out sensor analysis [164, 174] of general organoleptic evaluation of the cheese structured semi-product taking into account that the elaborated cheese structured semi-product based on the defrosted nonfat lactic cheese is a new product in a present-day foodstuff market, with the account of limiting deviations in functioning of A, B, C, D subsystems (fig. 3.1) for the obtaining of the product with similar quality by means of the experts on the grounds of sensor assessment scale and with the account of the ponderability coefficient.

During the sensor researches of the fresh cheese structured semiproduct based on the defrosted nonfat lactic cheese it was determined that the most important for the formation of organoleptic parameters of the named product are homogeneity and glossiness of the surface, natural color, fragility and porosity, continuity and plasticity of the structure, purity, naturalness, expressiveness, liberalization of flavor and aroma, and their balance.

Table 3.15

Development of the scale for sensor evaluation of a cheese structured semi-product

Table 3.15 continued

Om the profiles of organoleptic evaluation presented as a fixed area, the importance of each of parameter within the concise characteristics is emphasized (fig. 3.4)/

Table 3.16

Table 3.16 continued

	2	3	4	5
Flavor		Pure	5,0	5,0
	2	Natural	5,0	4,5
	3	Expressed	4,5	4,0
	4	Balanced	5,0	4,5
		Rate of liberation	4,0	3,5
Texture		Plastic	4,5	4,0
	$\overline{2}$	Elastic	3,0	3,0
	3	Continuous	4,0	3,5
	4	Greasy	1,0	1,1
	5	Juicy	2,0	1,5
	6	Sticky	0, 5	0,5
		Fragile	2,5	2,0

The investigations of organoleptic parameters of a cheese structured semiproduct during storage at temperature +2…6° С for 28 days in a consumer container – lidded polymeric jars (fig. 3.5) showed that the texture slightly changes, intensity falls but the rate of the aroma and flavor liberation grows.

Fig. 3.4. The profiles of organoleptic evaluation of a fresh cheese structured semi-product based on nonfat lactic cheese

Fig. 3.5. The profiles of organoleptic evaluation of a cheese structured semi-product based on nonfat lactic cheese after 28 days of storage

The structured cheese semi-product based on nonfat lactic cheese with the change of milk fat to plant purified deodorized oil is a new food product in the existing assortment of traditional structural products and can be used in common diet both separately and as the component of culinary products [72, 220].

Fig. 3.6. Assortment of culinary products with the use of a cheese semifinished product

Fig. 3.7. Process chart of cooking "Gretska gora" salad

Fig. 3.8. Process chart of cooking pork steak "Povna torba"

Fig. 3.9. Process chart of cooking the appetizer «Cheese plate»

Fig. 3.10. Process chart of cooking «Cheese» toasts

Confirmation of the statements of the elaborated innovative strategy and effective hypothesis (chapter 2.10) on the results of the implementation of a complex of analytical and experimental investigations (chapters 2.2 and 3.1-3.4) allowed to develop the technology of a cheese structured semi-product based on defrosted nonfat lactic cheese with the use of sunflower seed kernel concentrate. From technological point of view, it was planned to use the developed cheese structured semi-product in a mixture with other ingredients and independently as a component of culinary products.

Based on the generalization of the results of research, culinary products with the use of a cheese structured semi-product is elaborated. The assortment of the products and some structural schemes of products are presented in tables 3.6-3.10.

The composition of the recipe and cooking technology are worked out during technological developments. Process charts for the developed culinary products are adopted in accordance with the established procedure.

Summing up the results of the investigations it is worth noting that the use of a cheese structured semi-product as a component of culinary production allows to extend its assortment, suggest the products with new consumer properties, with the increased nutritive value, to raise functioning of restaurant business enterprises.

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