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TECHNOLOGIES OF FOOD PRODUCTS ON THE BASE OF MILK PROTEIN

The monograph

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The monograph provides concentrated and comprehensively systemized scientific information concerning the use of milk protein in culinary production at restaurants. It is offered in text, technological calculations, figures, flowcharts, and tables to instructors and students engaged in scientific research.

This edition has noteworthy visual illustrations, a list of technical questions, and recommended scientific-methodical references for process engineers, who work in the dairy processing industry and wish to improve their knowledge in this scientific area.

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CONTENTS

Preface

The present state of development of the food industry and restaurant catering challenge the specialists to develop and apply efficient and competitive technologies of a wider range of higher quality and nutritional value food products with improved consumer characteristics.

In the market economy, the consumer demand controls the development of the assortment of marketed foods. The problem of satisfying the consumer demand in foods of high nutritional and biological value is of drastic importance at the present stage of the new technological development marked by the availability of a significant unused raw material potential.

Recent years have seen a growing interest in milk and dairy products, which are the most valuable in nutritional and biological sense, and are widely used as ingredients in various formulas and recipes.

It is only natural that considering the protein deficiency in the diet, the most important role in a wide range of dairy products belongs to milk proteins, since they have high nutritional and biological value. They are balanced in the most essential substances for human, which ensure organism's growth, development, and activities.

This is the reason why scientific research works of theoretical and practical nature concerning complex obtaining, processing, and use of milk proteins have become so acutely popular. The issue interests many Ukrainian and foreign researchers. Several methods of obtaining milk proteins have been proposed and substantiated by Prof. P.F. Diachenko. They are still widely used not only in this country, but also abroad. A.F. Zatyrka, V.M. Kozlov, L.I. Karpunina, P.V. Gurskii, whose works are aimed at the use of milk proteins in culinary production, have contributed to the issue.

Significant changes have taken place in the recent years in technologies and techniques of manufacturing dairy products. Brand new methods and techniques of milk processing have been applied, which allow to raise nutritional value of dairy products.

Taking these facts into consideration and following modern trends and recent changes, the studies of milk processing are of acute current importance for the development of new food products.

The monograph contains the materials, which comprise the characteristics and the description of the complex processing of raw material (milk) and culinary production on its base.

Chapter 1 gives the general characteristics of milk proteins, investigates their physical-chemical, functional-technological, and structural-mechanical properties, presents the theoretical foundations of obtaining milk proteins.

Chapter 2 gives milk proteins' general characteristics and the analysis of their production methods. It gives the details of the thermoacid method of obtaining proteins. Their processing attributes, nutritional and biological values are defined here.

Chapter 3 presents the materials concerning the development of the technology of culinary products on the base of milk protein obtained by thermoacid method, the developed recipe composition and the technological process of curd cakes production on the base of milk protein, the investigation of the developed products' quality indices.

Chapter 4 presents the scientific substantiation of the snack pastes on the base of fat-free lactic acid curd with addition of purified deodorized sunflower oil as a fat component and agar as a structure-former. It describes the modeling of the thermal processing, defines the structural-mechanical characteristics of the snack pastes' model system and the effect of the ratio of main the components on their organoleptic attributes.

Chapter 5 is dedicated to the development of the recipe composition, the technology of the snack pastes on the base of fat-free lactic acid curd and the technology of the culinary products with the snack pastes. It presents the investigations of nutritional and biological value of the snack pastes, their consumer safety indices, terms and conditions of storage, the developed complex quality index, the modeling of the distribution of the relative quality coefficient depending on the optimal contents of the main recipe components and the thermal processing temperature.

We believe our work will be useful for process engineers, who work in the dairy processing industry, students, and teachers wishing to acquire more profound knowledge in this scientific area.

Chapter 1. General Characteristics of Milk Proteins

1.1 Nutritional and Biological Value of Milk Protein

Milk is a valuable food product, which has great importance for human nutrition, because milk and dairy products contain a full range of nutritive substances, including essential ones for human organism. It is a multi-component, balanced system with high nutritional, immunological, and bactericidal properties.

All substances contained in milk are easily and most fully digested by human organism (protein – 96%, fat – 95%, carbohydrates – 98%).

Milk is a source of nutritional proteins of high biological value. The overall content of proteins in milk ranges from 2.9% to 4.0%.

Proteins are the most important components of cow milk. They play a dominant part in the living organism's metabolism and in building its cells. Proteins are the essence of all living organisms and perform many functions: structural, transporting, defensive, catalytic, hormonal ones and others.

Milk proteins have a unique structure not found anywhere else. Their absolute utilization degree in human is 75%.

Milk contains three groups of proteins: casein – about 80% of all milk proteins, serum proteins – about 20% of milk protein substances, proteins of fat globules' capsules – about 1% of all milk proteins. Main fractions of milk proteins are listed in Table1.1 [2, 5, 6, 7].

Amino acids linked together by peptide bonds are the base of protein molecules. Milk proteins are characterized by optimal ratio of amino acids (especially essential) close to aminogram of proteins in human organism. We know more than twenty amino acids. Eighteen of them were found in milk protein, eight of which are essential, i.e. not synthesized in human organism.

Milk protein contains most of them (methionine, tryptophane, isoleucine, phenylalanine, valine, leucine) in much bigger quantities than proteins of meat, fish, or vegetable products. Milk proteins contain carbon, oxygen, hydrogen, nitrogen, phosphorus, and sulfur. However, nitrogen, phosphorus, and sulfur are the most characteristic of proteins.

Proteins contain both cyclic and acyclic amino acids: neutral, acid, and basic. Most of them are acid. Basic milk proteins contain rather a lot of leucine, isoleucine, lysine, glutamine acid, α_s–casein – serine and proline compared to globular proteins of other food products. Milk proteins are considered the proteins of full biological value according to their content and ratio of essential amino acids [1, 8, 9].

Table1.1 – Composition and Content of Protein in Cow Milk.

Proteins	Content in milk	
	g/kg	%
1	2	3
Caseins, total	**26.0**	**79.5**
including:		
α_{S1}- casein	10.0	30.6
α_{S2}- casein	2.6	8.0
β- casein	10.1	30.8
χ- casein	3.3	10.1
Whey proteins, total	**6.3**	**19.3**
including:		
α- lactoalbumin	1.2	3.7
β- lactoglobulin	3.2	9.8
blood serum albumin	0.4	1.2
immunoglobulins	0.7	2.1
proteose-peptones	0.8	2.4
Proteins of fat globule capsules	0.4	1,2
Total protein content	**32.7**	**100.0**

The research data of nutritional and biological value show that among a great range of food products milk and dairy products are ideal to supply people with fully valuable animal proteins.

A high amino acid score characterizes the biological value of milk proteins. They contain a significant number of essential amino acids. It is typical for milk proteins to have a high content of glutamine acid, and much more of it is contained in casein than in whey proteins. In addition, casein is characterized by a high content of proline, valine, and arginine [5, 6, 8, 9].

Casein of milk is a source of biologically active peptides, especially glycomacropeptides. Under action of chemosin, they separate from χ-casein and contribute to the formation of protein clots with a high degree of dispersity, which are a cause for a high rate of hydrolysis of α_s–and β-caseins.

The physiological properties of phosphopeptides, which separate from α_{s1}-casein in small intestine during digestion, and those of proteose-peptones, which form from β-casein are close to the physiological properties of glycopeptides. These fragments of caseins resist further proteolytic splitting, create soluble

complexes with calcium, and contribute to absorption of calcium and phosphorus in bowels.

During hydrolysis of milk proteins in the gastrointestinal tract exomorphines or morphine-like (painkilling) peptides may be created. In theory, it is believed that exomorphines enter blood and participate in changing the general harmonic background of organism. Researchers believe that during further enzymatic hydrolysis β-casomorphines, which are fragments of β-casein, may create hexapeptides and smaller peptides, which have properties of immune modulators, i.e. the substances, which stimulate the development of infant immune systems. They may increase phagocytic activity of macrophages and organism's resistance to some infections.

Some deficiency of sulfurous amino acids, mostly cystine, is characteristic of casein. However, they are abundant in whey proteins. Sulfur is present in whey proteins due to the presence of sulfurous amino acids – methionine, cystine, and cysteine. They affect proteins during their processing, e.g. denaturation and organoleptic attributes during thermal processing.

Whey proteins are characterized by a high content of two more of the most deficient amino acids: lysine and tryptophane. Thus, addition of whey proteins to food products' recipes contributes to increasing their biological value, which is characterized by the improved balance of amino acid composition.

The nutritional value of milk proteins rises due to the compounds of protein molecules with vitamins, especially B group vitamins, mineral substances – Ca, Mg, K and Na, as well as lipids, which improve digestion of some amino acids by human organism [3, 5, 6].

During the recent decade the researchers have studied the protein found in milk and called angiogenine. This protein contributes to the growth of blood vessels, increases healing effect on wounds and burns.

Thus, milk proteins are proteins of high nutritional and biological value by both their composition and content of amino acids, and their rate of digestion in the gastrointestinal tract, as well as by other important biochemical and physiological properties, which stress the importance of dairy products in diets.

1.2 Physicochemical Properties Of Milk Proteins

Physicochemical properties of milk as a unique polydisperse system are defined, primarily, by its components' properties and their interactions. In addition, it is milk proteins that have a great effect on the said properties.

Casein. Casein is one of the main representatives of milk. Its quantity in milk ranges from 2.1% to 2.8%. Elementary composition of non-fractionated casein is the following, %: carbohydrates – 53.1; hydrogen – 7.1; oxygen – 22.8; nitrogen – 15.4; sulfur – 0.82; phosphorus – 0.8.

Casein can be obtained by precipitation from skim milk during its souring to pH 4.6…4.7.

Purified casein is amorphous white powder without odor or taste. It is practically insoluble in water and soluble in weak solutions of alkali, salts of alkaline and alkaline-earth metals and mineral acids. Casein is a heterogeneous protein. It means that during electrophoresis it creates several fractions with different mobility, which differ in composition and properties [1, 2, 8, 9].

In solution, casein has a number of free functional groups, which determine its charge, the character of interaction with water (hydrophilic properties) and capability of entering into a chemical reaction.

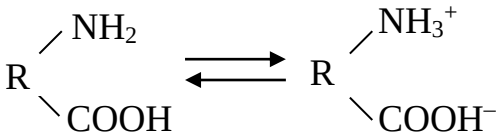
The ion form and molecular adsorption, which play an important role in hydration of protein molecules and stability of colloid of protein result from the presence of polar groups on the surface and inside of casein micelles ($–NH_2$, –COOH, –OH, etc.). Free polar groups of protein – carboxylic groups and amides, which are greatly hydrated, cause casein's ion form. The hydrated capsule consists of several layers, whose strengths of bonds with polar group decrease gradually with increasing distance from molecules of water to the centers of charges.

The first layer is oriented stationary molecules of water firmly bound with protein, i.e. the bound hydration moisture of molecular absorption. The rest of the layers are the moisture of poly-molecular absorption, which does not differ from free moisture under certain conditions. Bound polar groups of proteins – peptides, main polypeptide chains, hydroxyl, sulfhydric provide for molecular absorption as a result of the emergence of a charge due to the displacement of combined pair of electrons towards one of the atoms.

Polar groups of proteins usually bind ~1.9 g of water / 1g of protein. The capability of casein to bind water characterizes its hydrophilic properties, which depend on the structure, charge of a protein molecule, pH of a medium, the degree of reduction of protein substances, concentration of salts, and other factors [1, 7, 8].

When pH is 6.6…6.7, casein of fresh milk has negative charge. Equal positive and negative charges (isoelectric state of protein) appear in acid medium when pH is 4.6…4.7 (or 4.6…5.0).

Casein, like all proteins, contains at the same time amine ($–NH_2$) and carboxylic (-COOH) groups, which appear in a solution as NH_3^+ and $COO^–$. That means that casein has the properties of amphoteric electrolyte (ampholyte, amphion). The quantity of free carboxyl groups in casein is bigger than amine ones, because it has acid reaction:

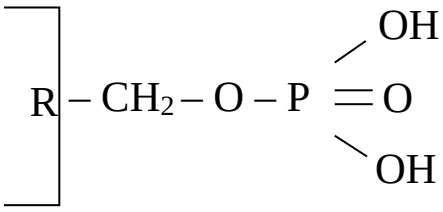


Casein has distinct acid properties in milk. Its free carboxylic groups of dicarboxylic amino acids and hydroxylic groups of phosphorus acid interact easily with the ions of salts of alkaline and alkaline-earth metals (Na^+, K^+, Ca^{2+}, Mg^{2+}), and create caseins. During iodination of tyrosine, which enters into the composition of protein, iod-casein is created. This is widely used now by the dairy and the bakery industries to fight against iodine deficiency of population.

Free amides of casein can interact with aldehyde, e.g. formaldehyde. This reaction is essential for determining protein content of milk by Formalin test method [1, 2, 8].

Casein is a compound of phosphoproteids (Figure 1.1.), which contain phosphorus acid residue (organic phosphorus), bound to amino acid of serine by monoester bond (O-P). As a result of many years of research it has been established that casein can be divided into the following main fractions: α_{s1}–, α_{s2}–β–,χ–-casein. The rest of its fractions are derivative [10-15].

All casein fractions are phosphoproteids, which contain different quantities of phosphorus acid residue. α_s-casein has eight residues of phosphorus acid in polypeptide chain, β–casein has four and χ–casein has one. This determines their sensitivity to ions of calcium. α_s– casein and β–casein are the most sensitive to ions of calcium. They form calcium bridges, aggregate, and precipitate [1, 2, 7].



Casein Serine Phosphorus Acid

Figure 1.1. Fragment of casein (phosphoproteid)

The fractions of, α_{s1}–, α_{s2}–, β–, χ–casein are well researched. They can be separated in a pure enough form. Their amino acid composition is known. Their

structure is also partially known. In milk casein is present as colloidal solution of gel (parts of highly disperse substance are distributed evenly in liquid medium) in the form of caseinate-calcium-phosphate complex (CCPC), which is created by the compound of caseinate of calcium and colloidal phosphate of calcium [10-12, 17-24]. In a quiet state when acidity rises or when rennet is added, milk protein coagulates into gel (hard jelly-like system). During ageing the coagulate (gel) contracts and releases water (whey) with solute substances (syneresis) [10-12, 16, 23-27].

Fractions of casein are highly interactive proteins, which tend to associate (aggregate). In water solution with the presence of calcium monomers of fractions create associates of different shapes and sizes. Moreover, they interact among both themselves, and one with another. An association of caseins depends on temperature, pH, and ion strength of milk.

α_{s1}-Casein is the main component of protein (its molecular mass is from 22000 to 24000 daltons). It is the most electrophoretically mobile and sensitive to ions of calcium. It differs from other fractions by the contents of lysine, asparaginic acid, tyrosine, lower content of leucine, proline, phenylalanine, and the absence of cysteine.

β-Casein is not sensitive to ions of calcium at 4°C. At 35°C, it precipitates interacting with them. Under certain conditions it may hydrolyze affected by milk plasmin consequently forming fragments of β-casein, which had been formerly called γ-casein (its molecular mass is from 12000 to 20000 daltons) and components of proteose-peptones (their molecular mass is from 4000 to 14000 daltons). This results in the deterioration of technological properties of milk in prolonged storage. β-casein is characterized by higher contents of valine, leucine, and proline, lower content of alanine, asparaginic acid, and the absence of cysteine.

χ-Casein (its molecular mass is 19000 daltons) is different from other fractions in that it contains cysteine, an important quantity of threonine, alanine, a little methionine and glycine. It is phosphoglycoproteid, which is insensitive to ions of calcium and is situated on the surface of micelle of casein. That is why it has a defensive function as to α_s- and β-caseins. χ-casein contains carbohydrates. It is sensitive to rennet and dissociates under its effect into hydrophobic para-χ-casein (which precipitates) and hydrophilic glycomacropeptide (which stays in the solution and separates together with serum). χ-casein contains only one phosphoserine residue (it is possible that some components have two residues). Therefore, it hardly bonds ions of calcium, i.e. it does not lose its solubility in their presence. During

association with α_{S1}- and β-caseins χ-casein creates stable micelles and this way defends the latter from precipitation by ions of calcium [1, 2, 6, 7, 8].

Electron microscopic research has established that CCPC consists of spherically shaped micelles, which consist of smaller particles – submicelles. Scientists have offered several appearances of the models of casein micelles. We consider the model offered by G.N.Krus to be most rational [10, 24-26]. Her theory stipulates that casein micelle consists mostly of three kinds of submicelles (A)-α_s-casein + χ-casein, (B)-α_s-casein + β-casein, (C)-β-casein + χ-casein (Figure 1.2).

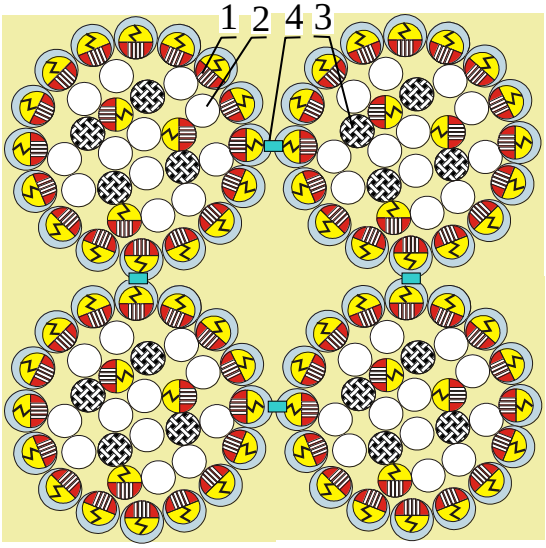


Figure 1.2 Model of Casein Micelle (according to Krus′):
1 - submicelle A (α_s- and χ-casein); 2 - submicelle B (α_s- and β-casein); 3 – submicelle C (β- and χ-casein, etc.); 4 – “calcium bridge”

The formation of submicelles (A) is carried out mostly due to hydrophobic and electrostatic interaction, as well as ions of calcium or colloidal calcium phosphate (CPC). Submicelles (B) interact with each other with the help of CPC and form a complex, which is the main part of a micelle’s nucleus. When it is formed submicelles (C) and some submicelles (A) interact with submicelles (B).

Submicelles are aggregated fractions of casein bound together by hydrophobic bonds and calcium bridges. Obviously, binding submicelles into micelles happens with the help of calcium phosphate and calcium bridges.

A micelle is finally formed when χ-casein content exceeds the critical concentration of micelle formation. In this case, χ-casein in submicelles A behaves as a typical surfactant substance. Submicelles (A) striving for self-association capture the nucleus and precipitate on its surface. At his time, bonds are created between submicelles (A) and (B) with the help of CPC, and the micelle’s growth stops. Submicelles (A) place themselves on the surface of the micelle in such a

way that N-end of χ-casein points inside the micelle and C-end of χ-casein stays on the surface. A great part of the micelle's surface is covered by C-end of χ-casein, which has thread-like, ramified because of carbohydrates structure. It forms the so-called "hair-cover» on the surface of the micelle. Sensitive to ions of calcium submicelles (B) and (C) concentrate inside the micelle [22].

That is, the submicelle is built in such a way that hydrophobic parts of casein molecules are hidden inside, and hydrophilic groups of χ-casein, which create hydrate capsules as thick as mono- or bi-molecular layer, are placed outside. Moreover, casein micelles have different polarity because of main and acid groups of atoms. Therefore, there are attraction and repulsion forces between micelles. Minimal repulsion forces are observed in isoelectric state of casein [17, 18, 22, 24-27].

Casein micelles have properties of hydrophilic sol, which can reverse to gel under certain circumstances. They are a colloidal phase of a compound composition, which has the properties of both hydrophilic and hydrophobic sol. In addition, very important for young organism salts of calcium, phosphorus and magnesium are transported in micelles.

Micelles have porous structure, because together with casein and non-organic components they contain much water – 0.7…4g of H_2O by 1g of protein. Rather little of this water (0.5g of water by 1g of protein) is bound by protein. It is the so-called "bound water." The rest of the water is immobilized (absorbed) inside micelles. The ratio between α_{S1}-, α_{S2}-, β- and χ-casein may be 3:1:3:1; 3:0.8:3:1, etc. The averaged physical parameters of casein micelles are given in Table 1.2 [1-3, 8].

Table 1.2 – Averaged Physical Parameters Of Casein Micelles

Parameters	Characteristic
Diameter, nm	130... 160
Area, cm^3	$8 \cdot 10^{-10}$
Volume, cm^3	$2{,}1 \cdot 10^{-15}$
Density (of hydrated micelle), kg/m^3	1063.2
Mass, g	$2{,}2 \cdot 10^{-15}$
Mass fraction of water, %	63
Hydration degree, g of H_2O by 1g of protein	3.7
Molecular mass of hydrated micelle	$1.3 \cdot 10^9$
Molecular mass of dehydrated micelle	$5 \cdot 10^s$
Number of peptide chains (with molecular mass of 30000) in micelle	10^4
Number of micelles in $1cm^3$ of milk	$10^{14}...10^{16}$

Casein is present in fresh milk in micelles of almost spherical shape. The average diameter of its particles is 70…100 nm (sometimes ranging from 40 to 300 nm) and the molecular mass is about 10^8. Further, casein micelles are comprised of subunits (submicelles) with the diameter of 8…15 nm and the molecular mass of 250000…300000 daltons.

Whey proteins. The term "whey proteins" commonly means the group of nitrogenous compounds of milk, which remain in milk plasma (whey) after the precipitation of casein at pH 4.6…4.7.

β-Lactoglobulin and λ-lactoglobulin should be considered as the main representatives of whey proteins. The former makes up about 50% (50…54%) of these proteins, the latter – about 20% (20…25%). The rest of whey proteins are albumin of serum, immunoglobulins, lactoferrin, and other minor proteins [2, 6, 7].

β-Lactoglobulin, λ-lactoglobulin and immunoglobulins perform important biological functions and are of great industrial importance due to the high content of essential and sulfurous amino acids. They are extracted from in negative state by ultra-filtration and used for enriching food products.

Albumin of serum is present in milk in small quantities and is of no practical importance. Lactoferrin, despite its small content, performs important biological functions and is essential for infant organism.

Besides the said proteins, whey contains components of the proteose-peptone fraction, which are fragments of β-casein, and other proteins, which have enzymatic and hormonal properties.

Unlike caseins, whey proteins do not associate with each other and do not precipitate in isoelectric point. Their molecular mass ranges widely from from 14.1 to 66.3 kdaltons and more. They show genetic polymorphism, polypeptide chains of protein molecules do not contain phosphorous esters, there are more sulfurous amino acids.

Whey proteins are characterized by even distribution of polar and nonpolar amino acids along the polypeptide chain, low content of proline, because they have a compact globular conformation with a significant spiralization of chains and average diameter from 15 to 50 nm. They are not hydrolyzed by plasmin and rennet. Compared to casein, they are less sensitive to calcium, but more sensitive to heating. Because of their small size, their number in milk exceeds the number of casein micelles about 1500 times.

β-Lactoglobulin stands for 50…54% of whey proteins (or 7…12% of all milk proteins). It has the isoelectric point at pH 5.1. In unboiled milk it is present as

dimmer, comprised of two polypeptide chains with molecular mass of 18 000 daltons each. When heated up to 30°C, β-lactoglobulin dissociates into monomers, which when heated further aggregate due to the formation of S-S-bonds:

$$R - SH + HS - R \xrightarrow[-H_2O]{+O} R - \boxed{S - S} - R$$

The thermal denaturation of β-lactoglobulin leads to coagulation of aggregated protein (it coagulates almost completely at 85…100°C).

During the pasteurization of milk the denatured β-lactoglobulin together with Ca $(P0_4)_2$ precipitates as part of milk sediment and forms complexes with χ-casein of casein micelles (precipitating together with them during the coagulation of casein).

The formation, as a result of heat processing, of the complex β-lactoglobulin - χ-casein impairs the attack on χ-casein by rennet and affects the heat resistance of casein micelles [1, 2, 8].

λ-Lactolbumin. In whey proteins λ-lactalbumin take the second place after β-lactoglobulin (its content is 20-25% of whey proteins or 2…5% of all quantity of proteins). λ-lactolbumin ahs the molecular mass of about 14 000 daltons. Its molecule is one polypeptide chain, which consists of 123 amino acid residues, which hold four disulfide bonds (-S-S-). For comparison, β-lactoglobulin molecule has two disulfide bonds and one free sulfide group (SH-group), which contributes to the quick aggregation after the denaturation.

Immunoglobulins. There is little quantity of immunoglobulins in common milk, whereas in colostrum they constitute the most part (up to 90%) of whey proteins.

Immunoglobulins join the group of high-molecular proteins, which have properties of antibodies. Antibodies are the substances, which are formed in an animal organism during the introduction of different foreign proteins (antigens) into it, and neutralize their harmful effect. Thus, the formation of antibodies is linked to the immune reactions of an organism. Milk immunoglobulins have distinct properties of agglutinins (L. *agglutinare* – to glue) - substances causing the agglutination and sedimentation of microbes and other cellular elements.

Milk immunoglobulins have greater molecular mass (150 000 daltons and more). They contain carbohydrates. They are thermolabile, i.e. they coagulate during heating of milk over 70°C [2, 3, 7, 8].

Lactoferrin is glycoproteid with the molecular mass of about 76 000 daltons containing iron. Protein has a transporting function – it binds and carries iron to

infant's organism, which especially needs it. In addition, it has defensive properties impeding the growth of the undesirable intestinal micro-flora (E.coli, etc.) by binding iron. Milk contains small quantities of Lactoferrin (less than 0.3 mg/g). Colostrum contains 10…15 times more.

Proteins of fat globule capsules. They comprise the proteins, which are the structural elements of fat globule capsules and contribute to their stability during technological treatment. They can be firmly built into the inside lipid layer of a capsule, pierce it or sit on the outside surface of the capsule. As a rule, it is glycoproteids with the molecular mass of 15000 to 240 000 daltons, which contain 15…50% of carbohydrates and have different solubility in water. Some of them have properties of enzymes. An important protein component of the capsule is hydrophobic (insoluble in water) glycoproteid with the molecular mass over 60 000 daltons. It is firmly built into the inside layer of a capsule and stays on the surface of fat globules during heat and mechanical treatment of milk (cream) [8].

The research and study of the physical-chemical, functional-technological, nutritional and biological properties of milk protein is of great importance for science and practical application in view of developing new products. Milk proteins' reaction to action of different agents is, to the minds of many authors, the theoretical base to use during the development and improvement of new methods of extracting proteins.

1.3 Functional-Technological Properties of Milk Proteins.

It is worth mentioning that milk proteins have the whole array of valuable functional properties (water-binding ability, viscosity, gel forming, emulsification, foam forming, etc.), which allow to use them as important components for developing various combined food products.

Hydration of proteins. Due to this property, milk proteins have moisture binding and water retaining abilities, which affects not only consistency and structure of a finished product, but also the production technology, and storage capabilities of such products as, e.g. various kinds of cheese.

Of great practical importance from the technological point of view is casein's ability to bind water. Under certain conditions, casein can bind a substantial quantity of water – about 3.7g by 1g of protein. The hydrophilic properties of casein depend on the structure, molecules' charge value, pH of environment, concentration of salts in it, and other factors.

The hydrophilic properties of casein are the base of stability of protein micelles in fresh, pasteurized and sterilized milk. It contributes to its growing thermal stability, which allows to heat milk not only up to the temperature of

pasteurization (72…95°C), but also up to the temperature of sterilization 143°C without its denaturation. During high temperature processing of milk casein's hydrophilic properties increase due to its interaction with whey proteins. The intensity of this interaction and the temperature have a direct effect on the structural-mechanical properties (strength, elasticity, release of whey) of a clot when producing lactic acid curd. Casein's hydrophilic properties also define water-binding and moisture retaining ability of finished product.

Casein's hydrophilic properties define not only the stability of protein particles in milk during its heat treatment, but also affect some technological processes.

The formation of water-binding and moisture-retaining abilities as a result of the interaction in the "protein-water" system is one of the most important functions of milk. The speed and stability of water-binding mostly depends on the state, properties and concentration of protein substances. The moisture-retaining ability of proteins is greatly influenced by their natural properties: the presence of charged polar and free polypeptide groups; the space structure of protein; the area of the questioned surface of protein particles. The conditions of hydration also have a great influence: the pH value of environment, which characterizes the level of ionization of amino groups; the degree of denaturation changes, which contribute to lowering sorption of water by protein due to the growing inter-protein interaction; the concentration and properties of electrolytes in the fluoric salts systems [1, 3, 6, 9].

Coagulation of proteins. The proteins' ability to coagulate and denature is used in the production of the cultured milk products.

Milk proteins are present in water solutions as colloidal particles, the sizes of which ranges from 1 to 200 nm. The stability of colloidal systems is conditional on a hydrate capsule and the presence of electric charges on the surface of the particles. The change of an electric charge and a breaking of the hydrate capsule cause precipitation (coagulation) of the particles. Globular proteins, including casein, obtain the excessive negative charge in solutions due to the predominance of acid amino acids residues in them. Under certain conditions (heating of milk, increasing concentration ions of hydrogen and calcium due to addition of acids and calcium chloride) casein's negative charge can be lowered. The pH value, which is marked by the balance of positive and negative charges is called *isoelectric point*.

For casein the isoelectric point is at pH 4.6…4.7. At this value of the pH the protein particles lose their ability to move in the electric field. The hydration of casein under these conditions is weak, and its lowest stability is observed. The

forces of electric repulsion between the protein molecules are minimal. This causes the proteins at isoelectric point to aggregate (enlarge) and coagulate (precipitate). During the coagulation there is a reverse precipitation of proteins, i.e. under certain conditions they can be converted into negative state again. Casein's property to precipitate at isoelectric point is used in all cultured milk products and cheese production [8, 9].

Denaturation of proteins. One of the most important properties of whey proteins is their denaturation. It may be caused by:

- high temperature;
- pressure and shear stress;
- ultraviolet or ionizing radiation;
- enzymes, organic solvents (alcohol, acetone), chemical substances, which react with functional groups on the surface of protein, and other factors.

The denaturation is a change of the structure of protein compared to its native state. The result of the denaturation is the unfolding of the tertiary and the secondary structures and the freeing of the functional groups inside them. The breaking of the hydrophobic bonds, which support the tertiary and the secondary structures of proteins, causes the unfolding of the specific native structure of protein molecules and building a free configuration. The bonds, which have supported the structure before, are free now and can orient themselves anew. Thee functional groups, which at the beginning were set inside the protein globules, and now also take part in forming the new bonds, start interacting with other protein molecules. In this process protein loses solubility, aggregates and coagulates.

The thermal denaturation acts mostly on whey proteins, which are the most thermolabile among milk proteins. During pasteurization and sterilization they undergo comparatively serious changes. First, their denaturation takes place, i.e. conformational changes of their protein molecules with breaking the tertiary and the secondary structures, as a result of which a compactly coiled molecule transforms into a chaotic skein; then follows the aggregation of the denatured particles due to the interaction of SH-groups:

$$R - SH + HS - R \longrightarrow R - S - S - R + H_2$$

The denaturation of most of the whey proteins begins at comparatively low temperatures of heating – between 62 and 78°C. The degree of denaturation (and aggregation) of proteins depends on the temperature, duration of milk's exposure and a solution's pH [1-4, 7-9].

The thermolabile whey proteins are capable of precipitating affected by an acid at Ph 4.6…4.7 after a preliminary thermal treatment of milk or whey (by boiling during 30 min). Only a negligible part of whey proteins are among those thermally stable milk proteins, which do not coagulate under the influence of a preliminary thermal treatment at pH 4.6.

It has been researched that the thermal treatment of milk at 85…87°C during 5…10 min and at 93…95°C during 2…3 min causes almost complete aggregation of denatured particles of whey proteins [22].

It has been established that the optimal modes of coagulation for the maximal output of proteins are the following: pH 4.4…4.6; temperature 90°C, duration 240 sec. The output of proteins is 93% [29, 30, 31].

Agraval S.P. and H. Piter (Germany) report that heating up to 90°C causes the denaturation of up to 60% of whey proteins [32].

The author [33] believes that whey proteins denature practically completely when milk is heated up to 100°C.

The research of the degree of the denaturation of whey proteins at different temperatures and during various holding periods have established that whey proteins denature completely at 95°C during 30 min [34].

From the presented data it is obvious that the most complete denaturation of whey proteins takes place at the temperatures 91…95°C, though we have to take into consideration the undesired changes in milk exposed to heat for a long duration.

The changes taking place can be explained by the fact that the inert functional groups of protein chains (sulfide, phenol, hydroxyl, etc.) in native proteins enter chemical reactions actively. This conditions molecular interactions in denatured proteins, and their molecules' ability to aggregate and form new complexes with other proteins, namely casein [35, 37].

Freeing SH-groups in milk due to thermal treatment begins at 75°C. Researchers in a number of works note that the interaction of whey proteins with casein takes place, if more than 50% of whey proteins denature during thermal treatment of milk. Nevertheless, in this case milk's ability of rennet sedimentation deteriorates [34, 36, 38, 39].

The most thermolabile proteins among whey proteins are immunoglobulin and albumin. β-lactoglobulin and λ-lactoglobulin are the most thermally stable proteins. The thermal denaturation of β-lactoglobulin causes the coagulation of aggregated protein (it coagulates almost completely at 85…100°C). Besides, β-lactoglobulin forms complexes with χ-casein of casein micelles and precipitate

together with them during the coagulation of casein. This complex greatly decreases the effect of rennet on χ-casein, and decreases milk proteins' thermostability.

The thermal denaturation of β-lactoglobulin goes on along the usual lines: unfolding of protein molecules – aggregation of denatured protein.

The thermal denaturation is a four-stage process. During the first stage, when milk's temperature rises up to 40°C and higher, β-lactoglobulin's dimer dissociates into two monomers. The further rising of the temperature (up to 70°C and higher) during the second stage is accompanied by the conformational changes β-lactoglobulin's of monomers: the molecules unfold gradually freeing SH-groups. The presence of one SH-group for one protein molecule is very important for third stage of the thermal denaturation process takes place at the temperature over 75the following reactions, which contribute to forming aggregates of β-lactoglobulin, and this way prevent the recurrent folding of polypeptide chains. The °C and is characterized by forming small size protein aggregates with the help of S-S-bonds. During the fourth stage, which is much slower than the third, comparatively large aggregates are formed from small ones [1, 2, 7, 8]..

After heating at not very high temperatures (70…80°C) only a small part of denatured (unfolded) molecules of β-lactoglobulin will be able to reconstruct their native structure. The reversibility of denaturation is likely to depend on the temperature and duration of heating.

At temperatures higher than 135°C the destabilization of the residual β-lactoglobulin structure takes place, i.e. a complete irreversible unfolding of polypeptide protein chains is observed.

Immunoglobulins, which denature at over 70°C, are also thermolabile.

The most thermostable among whey proteins is λ-lactoalbumin. Is necessary to heat milk up to 114°C for its complete coagulation. Nevertheless, the temperature of the protein denaturation is only 62°C. λ-lactoalbumin's great resistance to heating is explained by the denatured protein's reversibility; after cooling the reconstruction of its negative structure due to the involuntary re-coiling is observed (Figure 1.3). This process is called *renaturation*. The reversibility of denaturation at pH 6…7 is about 90% [1, 7, 9].

As a rule, globular proteins tend to aggregate after the thermal unfolding of molecules. It prevents the recurrent folding of polypeptide chains during cooling.

Many authors think that the high degree of renaturation of the thermally denatured λ-lactoalbumin can be explained by the protein's ability to stabilize its tertiary structure with the help of calcium. λ-lactoalbumin is metalloproteid, which

binds a certain quantity Ca^{2+}, isolation of which is accompanied by the conformational change of protein structure and substantially slows down the renaturation. Obviously, during the thermal unfolding λ-lactoalbumin loses calcium, which joins protein again during cooling and contributes to the reconstruction of its tertiary structure.

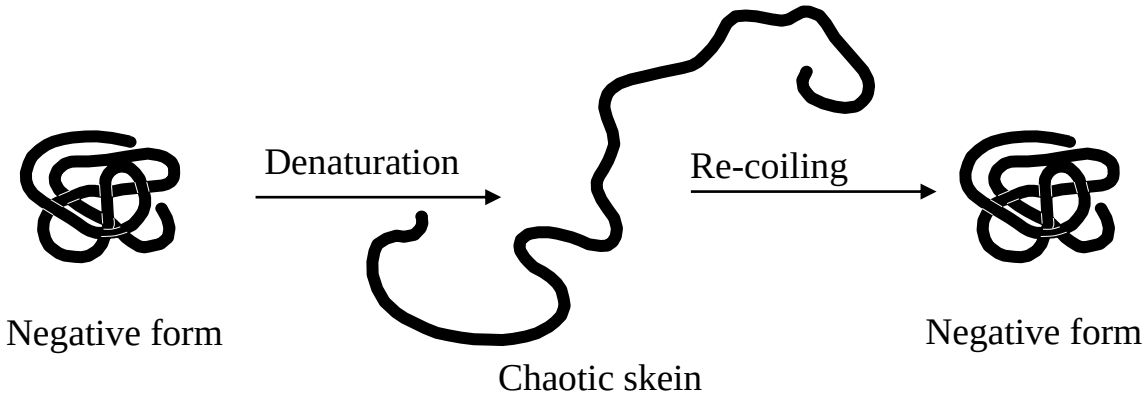


Figure 1.3. Re-coiling of λ-lactoalbumin chains

Unlike common globular proteins, casein has very high thermostability. Such high thermal stability of casein is due to a specific structure of protein (high content of proline, absence of free sulfhydryc groups, etc.), which has all denaturation features in native state already. The experimental data show that during heating at 140°C casein does not manifest endothermic effect, which is characteristic of the process of the unfolding of the globular proteins' structure.

Hydrolysis of milk proteins. At the same time during the thermal treatment, especially at high temperatures of sterilization, quite a number of physical-chemical changes, which may negatively affect the technological properties and nutritional value of milk, takes place in caseinate-calcium-phosphate complex. For example, the hydrolysis of peptide bonds, dephosphorization, dehydration of casein, its complex formation with denatured whey proteins, lactose, etc. may take place. These processes may result in disintegration of casein micelles or, vice verse, increase of their size, which cause the deterioration of rennet precipitation of milk, coagulation of proteins during storage of dairy products, etc.

During the disintegration of proteins the hydrolysis of peptide bonds takes place. It results, first, in formation of proteoses, peptones, polypeptides, oligopeptides, then amino acids, and finally, the secondary products of disintegration – ammonia, amines, hydrogen sulfide. The breaking of peptide bonds and formation of free amino acids during the hydrolysis (breakdown) of

polypeptides plays a great role during the ripening of cheeses, and in cultured milk products production [1, 8, 9].

The casein hydrolysis (especially, χ-casein hydrolysis, and to a less dergree α_s- and β-casein hydrolysis) during freeing different peptides caused by the effect of high temperatures on milk is mentioned by many authors. Thus, for example, the freeing of glycomacropeptides is observed as a result of the hydrolysis of peptide bonds in χ-casein at 100…114°C.The degree of hydration of casein micelles decreases in this case. As research shows, the thermally split glycomacropeptides are similar to glycomacropeptides freed by the action of rennet on casein. As we know, χ-casein plays a great role in stabilization of casein micelles, during thermal treatment included. Thus, the hydrolysis of about 20% of all casein may cause thermal coagulation of milk proteins.

The thermal dephosphorization of casein, i.e. the hydrolysis of phosphorus-ester bonds with the extraction of a part of organic phosphorus from β-and α_s- casein may decrease the aggregate negative charge of casein micelles and cause electrostatic current in the system. The dephosphorization of casein takes place at temperatures higher than 100°C. After the dephosphorization of casein, its ability to bind calcium, a part of which goes out of calcium caseinates, degrades. The destabilization of micelles, as well as their polarization follow. It means that in the end the thermal stability of proteins decreases [1-3, 6-8].

Milk proteins complex forming. The ability of casein (mostly χ-casein, and probably a_s- and β- casein) to form complexes with denatured whey proteins is of great practical interest.

The complex formation begins at comparatively low temperatures (80…95°C). The percentage of whey proteins (mostly β-lactoglobulins), which join casein, does not depend so much on the temperature, as on the duration of thermal treatment and may be 42…68%. Disulfide bridges are considered to be the main kind of bondage, which contributes to forming protein complexes, though, the participation of other kinds (hydrofhobic, etc.) is not negated.

It is obvious that the degree of interaction of β-lactoglobulin with casein, which is determined by their correlative content in milk, temperature, and pH of treatment, affects casein micelles' size. Most of researchers point out the increase in average size of casein micelles after thermal treatment of milk as the outcome of aggregation, association of casein with denatured β-lactoglobulin; as well as the precipitation of calcium on the surface of colloidal phosphate micelles. Nevertheless, some of the authors point out that in the process of heat treatment along with the increase of the number of casein micelles there is a substantial

increase in the quantity of very small particles, which signals the disintegration of micelles. However, the process of aggregation of casein particles and increase in viscosity of milk prevails [1, 7-9].

Foam forming capability. Milk proteins also have foam forming capabiliity, if they are conditioned with alkaline or enzymatic preparations of certain concentrations. This property is used in production of finely porous foam products, e.g. ice-cream [9].

Emulsification capability is seen only in solutions. That is why the important characteristics for proteins are hydration and solubility. The most important function of proteins is their capability to be absorbed on the interface with the orientation of hydrophobic and hydrophilic areas towards homogeneity with the environment. This capability depends on the values of active acidity pH, ion strength, and temperature. The stabilization capability of emulsions water/fat and fat/water for proteins is based on the capability to form on the interface strong absorption layers. They play the role of structural-mechanical barrier preventing coalescence of fat phase and contributing to increasing the environment viscosity, which decreases the effect of G-forces on the emulsion's stability and density [2, 3, 9].

The functional-technological properties of milk proteins include some specific properties, which play a certain role in technological processes of dairy products manufacture, notably thermal stability of milk, rennet precipitation, etc.

Thermal stability is milk's capability to withstand heating at high temperatures without visible protein coagulation. The main markers of stability of protein molecules in solution is a surface charge and a degree of hydroscopic property of particles. Thus, the factors, which decrease the negative charge of casein micelles and the degree of their hydration, will decrease the thermostability of milk.

They include the quantitative and qualitative changes of the chemical content of milk and, first of all, of fraction compounds of casein, the degree of the denaturation of whey proteins, the salt content and pH of milk. The differences in contents of milk depend on the season, lactation stages , kinds of cows, nutrition rations, etc.

The important role in demonstrating this property belongs to casein. There is no evident change in casein when heating fresh milk up to 120°C. When milk is heated up to 130°C during some time casein coagulates. Due to this fresh milk may be subject to pasteurization and even sterilization, with no fear of precipitation of proteins.

The researchers consider one of the reasons of thermal stability of casein to be the high content of proline and a low content of sulfurous amino acids (cystine and cysteine) in comparison with the whey proteins.

The salt content of milk, the micelles' size and charge, as well as the degree of the hydration of its particles effect greatly the thermal stability of casein [3, 5-8].

The thermal stability of casein is determined mostly by its acidity and salt balance. It depends on the balance between cations (calcium, magnesium, etc.) and anions (citrates, phosphates, etc.). The excess of one or the other ruins the salt balance of the system, which may cause the coagulation of proteins.

The rennet precipitation is the capacity of milk to precipitate effected by rennet enzyme with the formation of a solid enough clot**.** The content of casein and ions of calcium effect the rennet precipitation of milk: the higher their content, the faster milk precipitates, and the denser is the formed protein clot.

The duration of the rennet coagulation of proteins and the density of the clot depend on the hydrogen ion concentration in milk. The reaction goes on quicker and the clot is denser when pH of milk decreases.

The rate of protein precipitation and the clot density depend on the content of casein in milk: the larger it is, the denser is milk, the faster the coagulation of proteins will take place and the denser the clot will be.

The changes of micelles' structure and size caused by the thermal treatment affect the quickness of obtaining the rennet clot. After the pasteurization at temperatures higher than 80°C and ultra-high temperature treatment at 135…150°C the duration of the rennet precipitation increases several times compared to the duration of the rennet precipitation of unboiled milk (sterilized milk practically loses rennet precipitation capability). The prolongation of the duration of the precipitation of milk (along with the change of the salt content) can be explained by the complex formation of the denatured β-lactoglobulin with χ-casein, as a result of which the attack by rennet enzyme is weakened.

The fat globules do not contribute to the formation of the good consistency clot. The more large fat globules are in milk, the less dense is the clot.

It is also worth mentioning that the coagulation and precipitation may be desirable as well as undesirable in milk and dairy products manufacture. The desirable kinds of coagulation and precipitation are those, which purposefully cause the following:

- rennet precipitation during souring of milk in cheese production;
- acid precipitation in sour milk drinks production;
- acid coagulation to obtain raw casein;

- acid coagulation to obtain milk protein co-precipitates.

The undesirable kinds of coagulation and precipitation are those that cause the deterioration of milk products quality, namely:

- thermal coagulation of fresh and condensed milk;
- jellying of condensed milk during its storage;
- coagulation of homogenized dairy products after ultra-pasteurization;
- coagulation of frozen and then defrosted milk.

The disintegration of proteins in unboiled milk is caused by native plasmin enzyme, proteolytic enzymes of milk micro-flora and added yeast.

During storage of unboiled milk, the negative protease pro-enzyme plasminogen transforms into plasmin, which causes the disintegration of β-casein forming γ-casein and phosphopeptides.

The degree and depth of splitting proteins of unboiled milk by microorganisms depend on many factors, the main ones among which are the content and activity of their proteolytic enzymes [1, 2, 8, 9].

So, the physical-chemical and functional-technological properties are closely connected with each other and with the content of milk, its organoleptic indices, nutritional value and, in a certain way, they determine the economic cost-effectiveness and productiveness of processing milk into specific dairy products.

1.4 The Theoretical Foundations of Milk Proteins Production

When producing dairy products different associated products are obtained (fat-free milk, buttermilk, whey). More than 50% of milk proteins remain in them. Thus, there must be found a way of their efficient use for the manufacture of food products. Fat-free milk is widely used for the production of milk proteins, which comprise casein and caseinates, casecin and coprecipitates (casein with whey proteins) in solute and undissolved forms, as well as whey protein concentrates [40-42].

According to E. Voss and D. Prokopek's (Germany) classification liquid and pasty milk proteins contain up to 80% of moisture and are divided into [43]:

- products containing casein and whey proteins (raw coprecipitate; proteins produced from fat-free milk by gel-filtration, reverse osmosis and ultra-filtration);
- products containing casein only (raw casein, liquid caseinate);
- products containing whey proteins only (concentrates of soluble and insoluble whey proteins).

According to the milk protein classification the methods of their production may be divided into:

- methods of extraction of principal protein – casein (acid, rennet, rennet-acid, ultra-filtration);
- methods of extraction of whey proteins (thermo-calcium and thermo-acid).

In addition, the methods of complex (casein together with whey proteins) extraction of milk proteins are used: thermo-calcium and thermo-acid [42, 44, 45].

At present there are many ways of extracting and processing milk proteins, which are at the base of technological processes of milk-protein products manufacture.

All of them are based on debalancing and destabilizing the colloidal system of milk, and have their advantages and disadvantages.

The acid coagulation takes place mostly because of lactic acid, which is stored in the process of lactic acid fermentation, or because of the acid introduced from the outside.

The present views of the acid coagulation are presented in a number of works [44, 46, 47].

Negative electric charges prevail on the surface of casein globules. The explanation is that carboxyl and hydroxyl groups prevail over amine groups. When lactic acid is introduced the hydrogen ions H^+ are gradually bound by the electrically charged groups COO^- and are neutralized. The number of negative charges on the casein globules' surface decreases and, in some time, the balance of casein particles' positive and negative charges is reached. As a result of neutralization of negatively charged groups in the zone of active acidity at pH 4.6…4.7, the casein particles lose their stability and aggregate. The coagulated casein particles join and compress. A space net with milk substances inside forms into a clot.

Whey proteins do not coagulate in the process of acid coagulation, because they cannot be denatured. They keep their native state and are extracted from the clot together with the whey [44, 45].

Arginine groups are freed during the hydrolytic splitting of phosphoamide bonds. The increase in alkaline groups causes the casein's isoelectric point to move from pH 4.6…4.7 to 5.0…5.2 and forming paracasein. On the other hand, the phosphorus acid hydroxyl groups bind calcium ions and form bridges between the paracasein particles, which causes forming rennet clot [42].

Rennet does not make whey proteins coagulate. They are extracted together with whey through the casein clot chains during syneresis.

Under the combined effect of rennet and lactic acid on casein, which takes place during rennet-acid coagulation, casein transforming into paracasein moves

the isoelectric point from pH 4.6 to 5.2. In this case the clot will form faster, than during the acid coagulation. The technological process shortens by 2…4 hours.

The list of the methods of producing proteins from milk have especially expanded due to the fundamental theoretical researches in the field of chemistry of proteins, namely milk proteins, which lead to developing new technologies. For example, the methods of thermocalcium and thermoacid precipitation of milk proteins to produce coprecipitates have become very popular [46, 48, 49, 50, 51].

Taking into consideration the fact that the high-temperature coagulation provides for the complex production of almost all protein substances contained in milk in the minimal time duration, it is necessary to search for the ways of its wider application to produce different kinds of milk protein products.

All technological processes of milk protein production are characterized by similar stages: 1) heating the raw material (fat-free milk) up to the desired temperature; 2) mixing with coagulant (calcium chloride or acid solution) in a certain ratio; 3) holding the mixture for forming and fixing a clot; 4) cutting the clot; 5) extraction of whey; 6) ablution of protein; 7) pressing; 8)salting; 9) prepacking; 10) cooling; 11) freezing; 12) storing.

In 1962 an experimental non-stop food milk protein production line processing 5000 liters of fat-free milk per hour was built [52].

The year of 1971 saw a high economic effect of the use of milk protein for sausage production. Therefore, the production and use of such protein is limited, because of the low stability of a wet product during storage [53, 54].

At that time two distinctive directions in the process of protein extraction from milk were known. They were presented in the 50-s: the acid extraction in the USA and the calcium extraction in the USSR [52].

The precipitation of protein by ions of calcium was first presented and theoretically grounded by Prof. Diachenko in 1953 [46, 55-57].

In many countries of the world milk protein is produced industrially by the method of thermal coagulation [46, 50, 58, 59, 60, 61].

Thermocalcium method of milk protein extraction is the following: milk (unskimmed and defatted) is heated up to 90…93°C, then a 40% solution of calcium chloride is added in the ratio of 0.15…0.2% to the whole quantity of milk being processed, while being continuously stirred. After a quick complex precipitation of protein substances of milk the resulting whey is poured out, and the protein mass is washed with water and slightly pressed [44, 46].

The heating of milk with the use of calcium chloride as a coagulant causes the coagulation of casein along with the coagulation of thermolabile whey proteins,

and ultimately, the formation of the complex of casein with whey proteins, and their joint sedimentation.

The essence of the thermocalcium coagulation of milk proteins is in the following: casein and whey proteins are present in milk in colloidal disperse state. Casein micelles have the properties of hydrophilic sol, which under certain conditions can transform into a gel. The electric charge on the globules' surface and the balanced state of cations and anions present in milk plasmacontribute to the stabilization of casein. When there is an excess of ions Ca^{++}, their interaction with OH^- groups of phosphorus acid present in casein molecules begins. The negative charge of particles decreases, and the balance of positive and negative charges causing the maximal instability of casein particles and its coagulation appears. Moreover, calcium chloride has strong dehydration properties and contributes to destabilization and coagulation of casein, because it decreases hydrate capsules around casein micelles [45].

The method's drawbacks are the presence of foreign smack in the resulting coagulate of milk proteins brought in by calcium salts; a feeling of compressed hard consistency of products, and sometimes, its graininess due to dehydration of protein mass; a more complicated technology of processing of the resulting product (malaxing it into homogeneous state, mixing with other components) because of its compressed consistency.

Moreover, when this method is used industrially, a great quantity of deficient reagent – food calcium chloride is needed for protein extraction. Because of calcium chloride's bitter taste, which transfers to whey after protein substances extraction, the latter cannot be used for food purposes. This is one more drawback of said method of milk protein production.

The process of calcium coagulation of milk proteins, i.e. the food milk protein production, was suggested on the base of the research performed by Prof. Diachenko. This milk proteins production technology began to be implemented in 1969 [55, 63].

Further research proved the feasibility and efficiency of the industrial application of the said method of protein production.

The research on the base of the theoretical works by P.F. Diachenko and K.K. Rostros is going on seeking to improve the technology of producing moist milk protein on the base of the calcium coagulation with the ultimate purpose of creating a non-stop protein production line.

The technology of production of milk protein with various calcium content by regulating pH coagulation and the quantity of calcium chloride has been proposed [53, 65].

The development of the method of milk protein calcium coagulation at high temperature is expounded in the works by Australian scientists. In 1964 they offered the industrial technology of non-stop food protein production using the equipment for line production of casein [50].

In 1952 Scott patented the method of thermo-acid coagulation of protein complex in the USA [66].

The authors Kozlov V.M., Zatirka A.F. et al. point that the thermo-acid method has found wide practical use in the dairy industry. The produced coagulates are used in food production [40, 45].

The thermo-acid method has a number of advantages over the thermo-calcium method. It allows the complex extraction of casein and whey proteins, and the final product does not have the earlier said drawbacks of organoleptic features.

The essence of the thermo-acid method of milk protein coagulation is that the quick, almost instant, milk protein coagulation is performed by introducing into protein the lactic acid gathered in the lactic acid streptococcus yeast during lactic acid fermentation, or the protein is present in whey obtained during curd production by acid or rennet-acid method.

The method of milk protein production from fat-free milk with the help of lactic acid was thoroughly developed by Muller [67, 68]. Defatted milk is heated up to 92°C and held 15 min for coagulation of whey proteins, then mixed with acid at pH 4.3…4.35. The obtained milk protein contains casein and whey proteins.

The process goes on like this. Milk (unskimmed or fat-free) is heated up to 91…95°C, but not lower than 90°C. Then 25…30% of the lactic acid streptococcus yeast or acid cheese whey is added. After the coagulation of protein substances the produced whey is removed, and the protein mass is slightly pressed and cooled. The use of the said method of protein substances extraction is no less effective than the method described before, though it is close to the natural forming of a milk protein clot, i.e. the traditional protein extraction by the acid method, as e.g. during lactic acid curd production [69].

Despite the said advantages, the compressed consistency of milk protein makes its use more complicated for manufacture of cheese products, pastes and creams, whose consistency must be tender without hard particles of compressed protein and graininess.

Other important aspect of the improvement of lactic acid products technologies towards fuller use of milk potential is raising milk pasteurization temperature.

The analysis of scientific literature [70, 71] indicates that in modern lactic acid curd production a lot of attention is paid to complex processing of milk with full use of all its components.

The improvement of technological processes of modern lactic acid curd production provide for the use of whey proteins along with casein. In this method whey proteins were precipitated together with casein and the ultimate complex was extracted from milk.

A West German firm Westfalia Separator proposed a method of lactic acid curd production, based on the whey protein extraction by high temperature processing of defatted milk. Milk is pasteurized at 85…90°C during 2..3 min to increase output of the final product. Raising the temperature of thermal treatment of output milk causes the change in the structure of whey proteins. During the following precipitation of milk about half of whey proteins precipitate together with casein, and output of cheese increases by 10%. However, during the high temperature treatment of milk the moisture retaining capability of produced milk protein clot increases, and it makes producing whey more difficult and complicated [72, 73].

Fuller use of milk proteins in lactic acid curd production can be achieved by the use of sour whey as coagulant [73].

The world is witnessing the growing production of milk protein. The leaders in production of casein and its derivatives are New Zealand and Australia. France, Poland, Check Republic, Slovakia, Bulgaria, Germany are also among the volume producers.

In many countries, especially in Australia and New Zealand, a lot of attention is paid to coprecipitate production [53, 74, 75].

A well-known Australian researcher, whose laboratory is engaged in new works on coprecipitates, reports that a whole new range of milk protein based products including coprecipitates has been created to satisfy the growing demand in high-quality protein. The latest achievements in the field of acid and rennet caseins, coprecipitates, caseinates, milk proteins, and whey protein concentrates production are reported. The author looks at various aspects of their production.

Several technologies of milk protein production have been developed and patented in Check Republic and Slovakia. One of is in precipitating proteins from milk by adding 0.1…0.2% of the chloride calcium solution at 80…100°C with the

following removal of whey and washing with cold water. Then 1…3% of joining calcium, sodium and potassium citrates or polyphosphate salts and the similar percentage of common salt are added to the precipitate. The product is textured and cooled. It allows for the 20% improvement of the milk protein use compared to the traditional methods of casein production. The output product has good moisture binding and emulsification properties, mixes well with other components [75].

According to another technology, milk is soured to pH 5.2…5.5, 0.2% solution of calcium chloride is added, and milk is heated during 10 min up to 85…90°C [75].

The method of casein or whey protein precipitation with the help of combined souring and heating for use in cheese production is patented in France [75].

The use of such methods of milk protein production as reverse osmosis, ultra- and diafiltration, and electrodialysis is hampered by high cost of equipment, its imperfection, low characteristics of membrane strength, difficulties of their regeneration and use of filtrate [76].

The realization of the method of milk protein production with the help of polysaccharides demands special equipment and is hampered by the deficiency of pectin [76].

The presented analysis of the milk protein production methods showed that the thermoacid method is one of the most promising and effective methods, which provide for the complex extraction of milk components. Thus, it is deemed essential to seek the ways of improving the thermoacid coagulation method to obtain the final product with the desired properties to produce various items on its base.

1.5 The Structural-Mechanical Properties of Milk Proteins

The basic protein components of casein micelles are α_{S1}-, α_{S2}-, β- and χ- caseins (Figure 1.2). The basic mineral components are calcium and phosphorus. Micelles contain a small quantity of citrate, magnesium, potassium, and sodium. The carbohydrate part of casein micelles is represented by sialic acid, galactose, and galactosamine. Calcium and phosphorus are held in casein micelles in two forms; non-organic calcium is a component of colloidal phosphate and calcium citrate, organic calcium is bound to phosphate and carboxyl groups of casein. Ions of calcium interact with the phosphorous acid residues joining its one or two hydroxyl (OH^-) groups. Besides, they join carboxyl groups (COO^-) of casein. In another case calcium has a free bond and can form a calcium bridge between serinephosphate groups of two casein molecules situated one opposite the other:

$$2R\text{-}COOH + Ca^{2+} \longrightarrow 2R\text{-}COOCa^{+} + 2H^{+};$$

$$2R\text{-}COOH + Ca^{2+} \longrightarrow R\text{-}COO\text{-}Ca\text{ -}OOC\text{ -}R + 2H^{+}$$

Such calcium plays a certain role in forming casein micelles and is called structure-forming, because it joins two molecules of casein. Calcium bridges contribute to the aggregation of colloidal particles of casein during rennet reaction and calcium coagulation. Phosphorus of colloidal calcium phosphate, similar to calcium, is considered non-organic, and phosphorus of casein – organic. Casein molecules may be joined as calcium bridges (Figure 1.2) by non-organic phosphorus of colloidal calcium phosphate, which along with ions of calcium may join casein molecules' serinephosphate groups.

According to Nemeta and Sheraga's calculations the hydrophobic interactions strengthen when temperature rises up to 60°C, then start weakening. At temperatures lower than 5°C the hydrophobic interactions will be minimal.

The interaction of oppositely charged groups under influence of electrostatic forces is usually of little significance for the stabilization of protein monomers and polymers. Water dipoles surround ionized groups in water solutions, and their interaction is weakened. However, the simultaneous attraction of many ionized groups during the interaction of protein subunit areas strengthened by hydrophobic environment can create a strong enough electrostatic stabilization of proteins or contribute to their aggregation.

Of a special interest are electrostatic interactions between phosphate and carboxyl groups of casein fractions with cation Ca^{2+}. Performing the role of a bridge uniting two phosphate casein groups calcium contributes to lowering its negative charge. This makes possible the hydrophobic interaction of submicelles, which contributes to their aggregation.

Hydrogen and disulfide bonds are present in submicelles in small quantities and do not influence micelle stabilization. Thus, the conclusion can be drawn that the hydrophobic interaction play the most important part in forming and stabilizing submicelles. The electrostatic interactions also are of a certain importance [1, 2, 4, 9].

1.6 Using Milk Proteins in Culinary Technologies

At present the dairy industry is greatly interested in a wide range of low prime cost products of high nutritional value. There is a growing producers' and consumers' interest in snack-type products of yielding viscous paste consistency. It is not feasible to use rennet curd as protein raw material for this kind of products due to delivery problems, high energy cost and high enough prime cost. Thus, milk proteins, e.g. lactic acid curd, sufficient quantities of which are supplied by most

dairy producers, are of special interest to restaurateurs as protein base in their culinary production technologies. Due its functional properties lactic acid curd can be used as basic protein raw material in plastic-viscous product technologies [77].

Lactic acid curd is a product of high nutritional and biological value due to a high enough protein and mineral substances (calcium, phosphorus, iron, magnesium, etc.) content essential to human daily nutritional needs. To increase lactic acid curd output by ~8% modern technologies make efficient use of direct addition yeasts (DVS-cultures) and CHY-MAX enzymes. This enzyme is characterized by 100% content of rennet (chemosin) as active enzyme having a splitting effect directed at χ–casein, due to which a quality clot is produced with the release of clear greenish whey without protein.

During curd production the protein coagulation (with breaking colloidal system of milk) takes place with lowering the negative charge of casein and its transformation into isoelectric state by adding separate or combined acids (acid coagulation), rennet (rennet coagulation), or calcium chloride (calcium coagulation).

The coagulation stage, the details of which have not been fully researched yet, is a biochemical reaction causing micelle aggregation. Here we may talk about hydrophobic bonds between para-χ–casein residues, salt bridges (calcium and calcium phosphate) between α_{s1},-, α_{s2}- and β- caseins, and possibly, about disulfide bridges between para-χ–caseins, etc. Micellar para-χ–caseins has a distinct hydrophobic character, i.e. due to a bio-molecular reation an output hydrophilic micelle obtains hydrophobic areas. This causes the appearance of a phase interface, and correspondingly, free (excess) interfacial energy, which according to Gibbs-Helmholtz principle, tends to decrease involuntarily in disperse systems, increases.

This process causes the reduction of the entropy of the system due to the increase of the part of the ordered elements in the structure of the surrounding water (the hydrophobic interactions between para-χ–casein molecules and water molecules are accompanied by the increase of the entropy and the transformation of the system into a more favorable energy state). Also favorable for the system is the joining of micelles into a unique compact structure, which ensures the least contact of hydrophobic areas with water. Concurrently the contacts between similar hydrophobic areas cause the reduction of the system's free energy.

It is worth mentioning that the chemical composition of lactic acid curd changes depending on its fat content (Table 1.30. Fat-free curd has ~6±2% more proteins than fatty curd.

Table 1.3 – Chemical composition of lactic acid curd

Lactic acid curd	Content, %				
	fat	moisture	proteins	lactose	sols
Fatty	18±1	65±2	14…16	1.9…2.1	1.5…2.0
Semi-fatty	9±1	73±2	14…17	2.0…2.5	1.7…1.5
Fat-free	–	80±2	18…22	1.5…2.0	1.3…1.6

The lactic acid curd produced in the non-stop mode on the base of protein coagulation in continuous line production has a somewhat poorer content of free amino acids (Table 1.4) [4] than the curd produced in the periodic mode. However, the former has a better moisture-retaining capability.

It is obvious that the difference in the free amino acid contents of the researched kinds of curd is due to the fact during the traditional curd production the yeast acts under better conditions and longer than during the lactic acid curd production in the coagulator. However, the free amino acid content in the curd produced by the non-stop method of protein coagulation in line can be increased by selecting the right quantity of bacterial yeast.

Table 1.4 – Amino acid content of proteins of lactic acid curd

Amino acid	Content in lactic acid curd produced by			
	periodic method, mg in 100 g		non-stop method, mg in 100 g	
	product	dry matter	product	solids
1	2	3	5	6
lysine	3.02	9.21	2.45	7.29
histidine	0.14	0.42	0.12	0.37
arginine	0.18	0.54	0.15	0.46
asparaginic acid	1.09	3.33	0.73	2.16
threonine	0.53	1.61	0.26	0.78
serine	0.68	2.07	0.27	0.82
glutaminic acid	6.42	19.57	3.46	10.31
proline	2.73	8.31	1.54	4.58
glycine	1.22	3.73	0.72	2.16
alanine	0.44	1.35	0.32	0.94
valine	0.36	1.08	0.22	0.64
methionine	0.35	1.05	0.20	0.60
isoleucine	0.49	1.49	0.13	0.38
leucine	0.23	0.69	0.14	0.42

1	2	3	5	6
tyrosine	0.88	2.69	0.53	1.59
phenylalanine	0.48	1.47	0.33	0.97
Total	19.23	58.61	11.57	34.47

The data in Table 1.4 also indicate the curd's high biological value, because of the presence of all essential amino acids (lysine, tryptophane, threonine, valine, methionine, isoleucine, leucine, phenylalanine) in its composition .

When characterizing the curd's chemical composition, it is worth taking into consideration its caloric value: 1kg of fatty curd has the caloric value of 2330…2530 kcal, 1kg of fat-free curd - 750…860 kcal, 1 kg of beef has the caloric value of about 1350 kcal, 1 kg of fish – about 460 kcal.

The lactic acid curd produced by the non-stop method contains on the average ~124.2 mg% of Ca and ~90.3 mg% of phosphorus. The lactic acid curd produced by the periodic method ~117.5 mg% of Ca, and ~77.0 mg% of phosphorus.

The lactic acid curd produced by the non-stop line production method of protein coagulation has the moisture-retaining capability 6…8% higher than the lactic acid curd produced by the periodic method. This probably happens because of a partial denaturation of whey proteins during milk pasteurization, which is 8…10% higher than during the periodic production (Table 1.5).

Table 1.5 – Dependence of moisture retaining capability of lactic acid curd's milk protein on pasteurization temperature

Lactic acid curd production method	Temperature of milk pasteurization, ^{0}C	Moisture-retaining capability of protein, %
Periodic	76…82	46…48
Non-stop	86…90	52…56

The interaction of denatured β-lactoglobulin with casein micelles takes place in the process of high-temperature treatment of milk. Whey proteins of milk have greater hydrophilic capability compared to casein. Thus, their moisture-retaining capability and thermal stability increases. Similarly, casein's hydrophilic properties effect acid and acid-rennet clots' capability to retain and release moisture. The change of casein's hydrophilic properties must be taken into consideration when choosing the pasteurization mode in the process of acid milk products manufacture, notably the production of lactic acid curd.

Lactic acid curd has thixotropic structure of coagulation type (capable of renewing after mechanical breaking). Between protein particles there are liquid globules, which give it plasticity and elasticity. The correctly selected strain composition of yeasts cultures allows regulating active acidity of a clot and keeping PH in the range of 4.5…4.8, which is important for producing a dense clot and forming a product taste.

The industrially produced lactic acid curd has the standard fat, dry substances, and moisture content. However, different batches of such lactic acid curd will have different ratios of fat mass to dry residue mass (DDMR- dry defatted milk residue), and of moisture mass to dry residue mass. That is why it is necessary to control the said parameters when lactic acid curd is used as an ingredient in snack pastes recipes.

Fat-free lactic acid curd, a basic product for paste-type products manufacture, can be regarded as concentrated suspension of casein particles in the solution of protein, salts and other hydrophilic substances. In industrial production the lactic acid curd as a basic raw material is an insignificant component part of the protein base of paste-type products. The fresh fat-free lactic acid curd improves the taste of cream cheese, increases its protein content, improves its consistency and raises active acidity. According to the traditional cream cheese production technologies the percentage of lactic acid curd in the formula is ~15…20% of all ingredients.

However, in the surveyed literature there is a lack of information about the use of lactic acid curd as basic protein raw material for paste-type snack products manufacture. Thus, we believe that the deficiency of milk raw materials makes the development of the paste production technologies with the use of lactic acid curd as basic protein raw material very challenging and promising.

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Chapter 2. Milk protein production technology

2.1 General Characteristics of Milk Proteins and the Analysis of Their Production Methods

Recently we have been able to witness a growing interest in the production of milk proteins produced from defatted milk or whey by the method of water, mineral substances, and lactose removal, as well as by way of combined concentration of proteins.

Depending on the mass quotient of dry substances the protein products produced from milk are divided into liquid, paste-like and dry. Further, inside each group they differ by kind and solubility in water (Figure 2.1) [1,2].

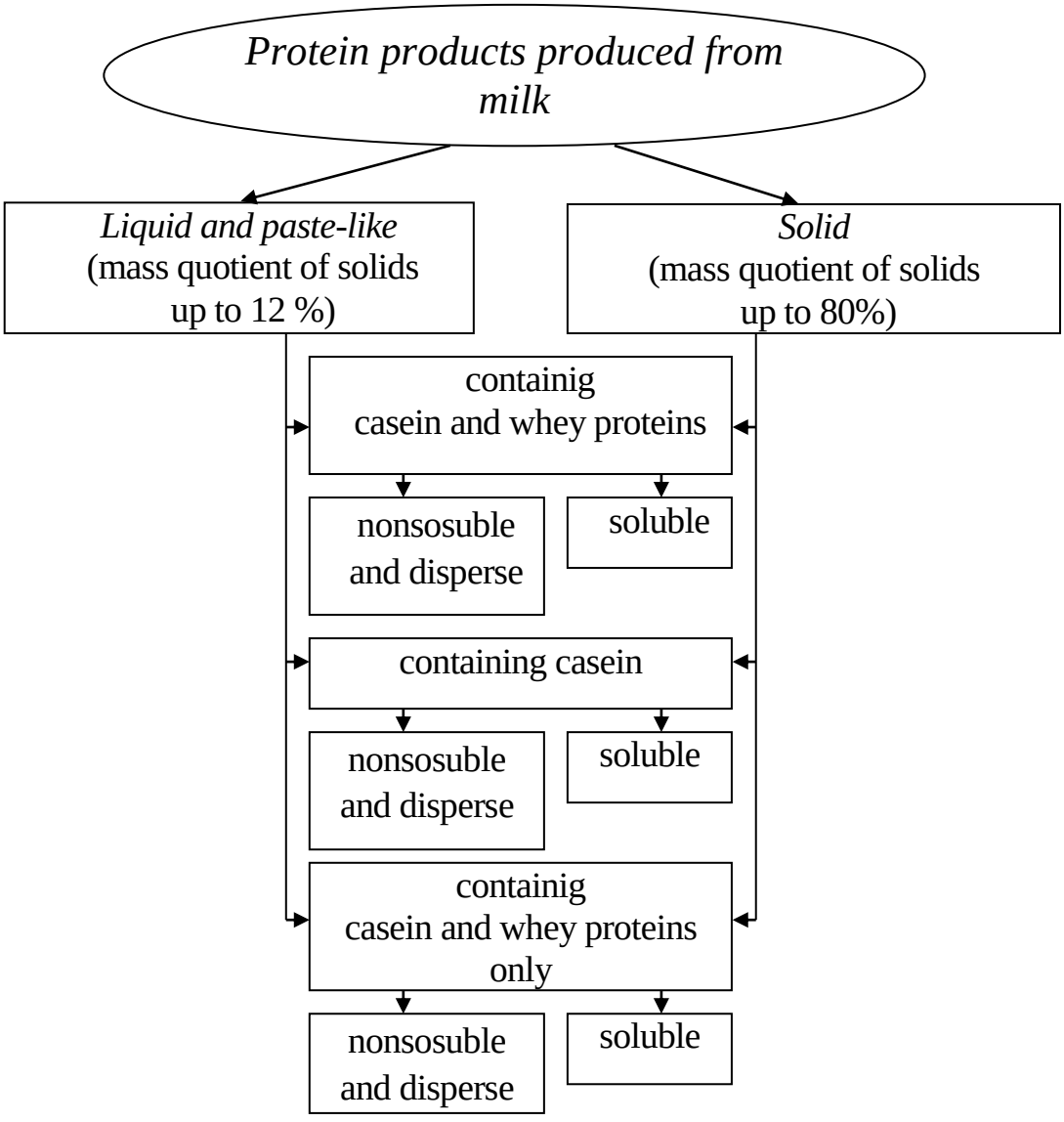

Figure 2.1 - Classification of milk protein products produced from milk

The term “disperse” means the types of milk protein products mechanically reduced to very small particles, while liquid was added, and turned into suspension, which does not precipitate.

Figure 2.2 presents the range of protein products [1].

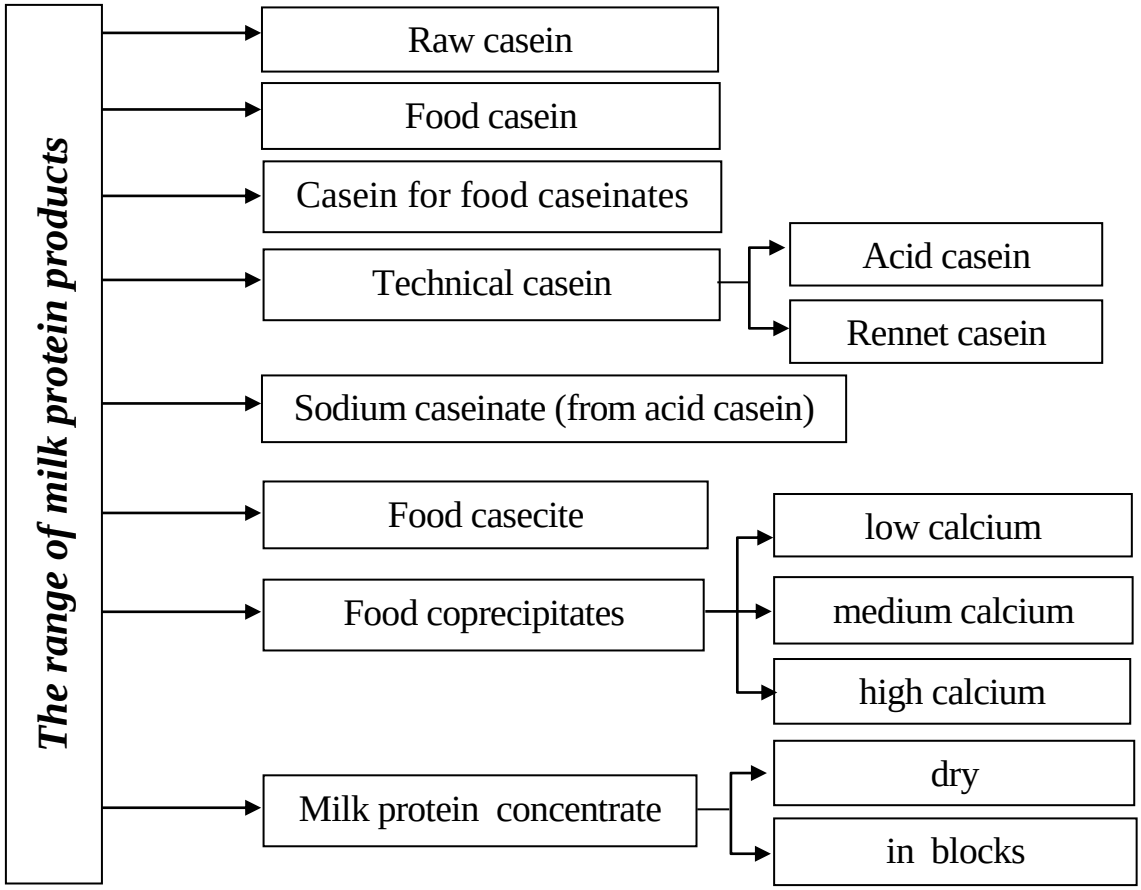

Figure 2.2 – Range of protein products.

Raw casein falls into the class of nonsoluble liquid, and paste-like milk protein concentrates, which contain casein only.

Food casein, casein for food caseinates, technical rennet casein are nonsoluble dry milk protein concentrates, which contain casein only.

Sodium caseinate and food casecite are soluble dry milk protein concentrates, which contain casein only.

Soluble food coprecipitates are soluble dry milk protein concentrates, which contain casein and whey proteins.

Milk protein concentrate in blocks are soluble liquid and paste-like milk protein concentrates, which contain casein and whey proteins.

Table 2.1 presents the physical- chemical indices of milk protein products [33].

Table 2.1 - Physical-chemical indices of milk protein products

Milk protein products	Mass quotient, %					Acidity, °T, not more than	pH	Solubility index, $см^3$ of moist sediment
	moisture not more than	sols, not more than	lactose, not more than	fat, not more than	protein, no less than			
Raw casein:								
Highest grade	65.0	0.8	0.4	0.55	32.0	25.0	-	Insoluble in water
First grade	65.0	0.8	0.4	0.55	32.0	40.0	-	
Food casein:								
highest grade	12.0	2.5	1.0	1.5	82.0	40.0	-	Insoluble in water
first grade	12.0	3,0	1.0	2.0	82.0	60.0	-	
Casein for food caseinates	12.0	2.0	1.0	1.5	82.0	70.0	-	Insoluble in water
Technical casein:								
acid tc: highest grade	12.0	2.5	1.0	1.5	82.0	50.0	-	Insoluble in water
first grade	12.0	3.0	1.0	1.5	82.0	90.0	-	
rennet tc: highest grade	12.0	7-8.5	1.0	1.5	78.0	50.0	-	Insoluble in water
first grade	12.0	7-8.5	1.0	1.5	78.0	70.0	-	
Sodium caseinate	6.0	5.0	1.0	2.0	85.0	-	6.2…6.9	0.2
Food casecite	6.0	7.0	2.0	2.0	80.0	-	6.6…7.0	0.2
Soluble food coprecipitates:								
low calcium	6.0	6.5	5.0	2.5	80.0	-	6.6…7.0	3.0
high calcium	6.0	14.5	5.0	2.5	75.0	-	8.8…7.1	5.0
Milk protein concentrate:								
dry	12.0	15.0	2.0	2.0	70.0	-	6,8…7,2	1.0
in blocks	55.0	7.0	1.0	1.0	35.0	-	6.8…7.2	0.95

The amino acid compositions of different kinds of protein products are presented in Table 2.2 [2, 3, 4]. The presented data show that whey proteins and coprecipitates are of higher biological value than casein due to a great number of sulfur amino acids.

Table 2.2 – Amino acid compositions of protein products

Amino acids	Average amino acid content, mg/g of nitrogen in*			
	casein	coprecipitates	soluble whey proteins	α-lacto-albumin
Isoluecine	332	338	367	369
Leucine	600	612	827	822
Lysine	505	503	658	595
Methionine	177	174	147	151
Sulfur containing	203	230	498	433
Phenylalanine	333	324	240	256
Cystine	26	56	351	282
Tyrosine	352	350	218	254
Aromatic	685	674	458	510
Threonine	268	272	361	319
Valine	397	406	352	374
Tryptophan	80	-	171	-
Arginine	241	225	184	198
Histidine	181	166	130	131

*Note: The nitrogen content, % to dry substances is: in casein – 15.05; in coprecipitate – 14.08; in soluble whey proteins – 10.8; in traditional lactoalbumin – 12.81.

Recently a lot of attention has been paid to milk and dairy products as the most nutritionally and biologically valuable; and they are widely used as ingredients of different dishes.

It is only natural that milk proteins play an important role in a wide range of dairy products due to the protein deficiency in diet, because they have high nutritional and biological value. They are balanced in the most essential for human organism substances, which ensure its growth, development, and vital functions [4,5].

Thus, there have been a great number of scientific research works focused on theoretical and practical aspects of studying and using milk proteins, their complex production and industrial processing [6, 7, 8].

The recent years have been marked by revolutionary changes in the technologies and techniques of production of dairy products; essentially new methods of milk processing have been introduced. The newly developed milk processing methods let increase the dairy products' nutritional value.

According to the scientifically substantiated principles of rational and balanced nutrition milk proteins are widely used industrially to increase the dairy products' nutritional value. New protein production technological processes and highly productive modern equipment have been created in many countries of the world. The leaders in production of milk proteins are New Zealand, Australia, the USA, France, Poland and some others.

At present, there are many methods of obtaining, concentration and technological processing of milk proteins, which are the base of the milk proteins products manufacture technological processes. Figure 2.3 presents the main methods of obtaining milk proteins.

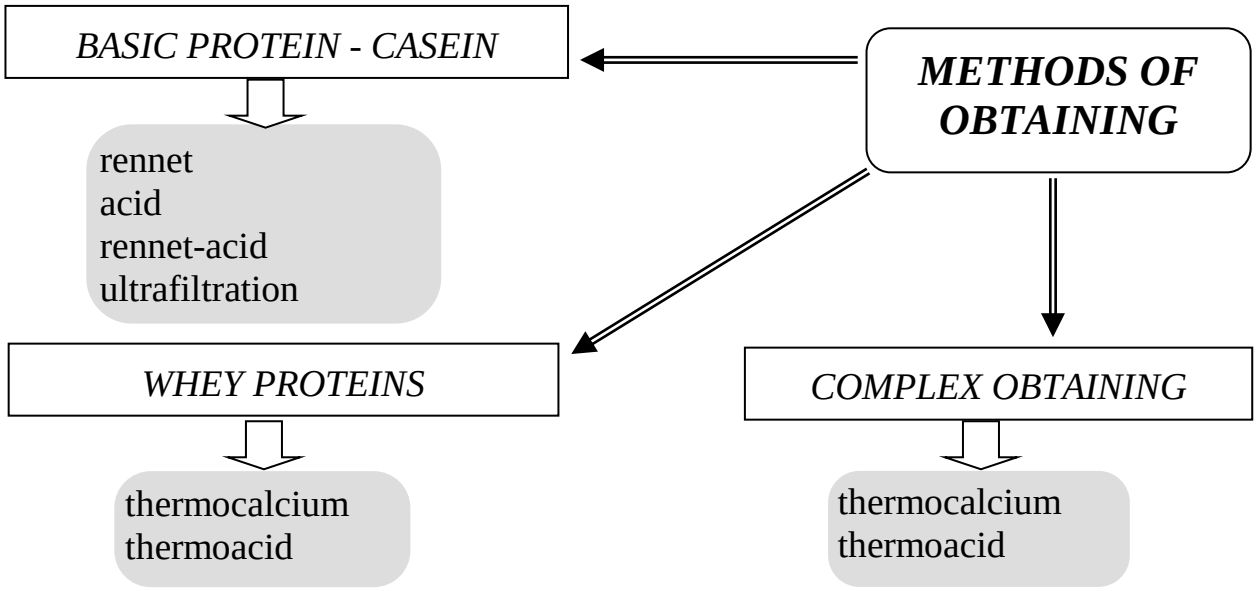

Figure 2.3 Methods of obtaining milk proteins.

As a result of complex method, casein is obtained together with whey proteins. Milk protein concentration can be done with other milk substances by condensation, drying or by membrane technology method.

The acid method of obtaining milk proteins, notably casein, has been known for a long time and is based on biochemical transformations of milk components. This method has been used in cheese production since long ago. It has also been used for obtaining acid casein, some cheeses and other milk protein products.

The rennet and rennet-acid method of obtaining proteins has been known since the ancient times. Its “discovery” was prompted by keeping milk in dried stomachs of animals, where it coagulated while remaining sweet. After some time people learned to produce various kinds of hard cheeses from the rennet clot, which had formed [2].

With the development of dairy production, technical equipment producers began to use milk condensation and drying methods to concentrate milk proteins along with other milk substances.

After finding whey proteins in whey released during hard and soft cheeses production, producers used different methods letting them to obtain parts of albumin and globulin.

Methods of obtaining whey proteins deserve special attention at present, because now it is particularly necessary to use protein substances of milk for nutritional purposes to the maximal extent.

This is the reason why the filtration methods of protein substances extraction from whey, as well as the thermocalcium and thermoacid methods of obtaining milk proteins are of such interest [1, 2, 4, 6].

Besides methods of extraction and concentration in milk protein products manufacture, the methods of processing of the obtained protein concentrates are used, as a result of which they acquire new organoleptic or functional properties, e.g. methods of deep splitting of milk proteins by fermentation.

The mechanical methods are based on mixing protein products with different components of milk and non-milk origin (sugar, salt, raisins, etc.). Such processing, for example, in cheese products manufacture, gives milk protein products new flavors and changes their chemical composition.

The physical methods are based, as a rule, on dehydration, e.g. such proteins as casein, coprecipitates and others.

The chemical methods due to protein products processing by various chemical agents (sodium hydroxide, etc.) give milk proteins new functional properties (emulsifying, moisture-retaining, foam-forming, etc.) [6, 9].

A more detailed analysis of the main milk proteins obtaining methods follows.

The acid coagulation is the most common method of obtaining milk proteins. It takes place mostly because of lactic acid, which accumulates during lactic acid fermentation or is added.

The essence of the modern conceptions of acid coagulation of milk proteins is the following. Milk casein has distinct acid properties. Thus, negative electric charges prevail on the casein globules’ surfaces. Due to lactic acid fermentation in

the system there is a gradual accumulation of lactic acid, which dissociates accumulating hydrogen ions H^+ and ions of residual $CH_3CHOHCOO^-$. As lactic acid accumulates in the system, the growing number of H^+ gradually neutralizes the casein globules' electric charges. When the electric charge on the surface is completely neutralized, the globule becomes electrically neutral, i.e. it is in the isoelectric point. This state comes at milk's pH 4.6…4.7. Now the casein's solubility, viscosity and swell are minimal. As a result of neutralization the particles lose stability and aggregate. It means creating the conditions for the irreversible coagulation. The isoelectric points of different casein fractions are different. They are 4.7; 4.9; 5.8; 6.0 for α-, β- and γ-caseins respectively. So, when milk is acidated to pH 4.6-4.7, all casein micelle's fractions coagulate completely. Under these hydration conditions whey proteins of milk (β-lactoglobulin and α-lactoalbumin) transfer to whey.

The acid coagulation may be tentatively subdivided into four stages. First, there is gradual neutralization of the casein globules' negative charges, the system becomes more and more unstable. Calcium, which splits from calcium-phosphate-casein complex, forms salts and this way transfers to whey. This stage is called induction period.

At the second stage the evergrowing number of casein globules become electrically neutral. They lose hydrate capsule. The aggregation of casein particles takes place. The protein coagulates. The massive coagulation stage is called flocculation.

At the third stage – the gel-forming stage, the casein particles, which have coagulated, join and compress. The structural linking takes place, all milk forms a clot. This is the clot compression stage.

At the fourth stage – the synerisis stage, the clot weakens and ruins. Its viscosity decreases. Whey releases [1, 2].

The acid coagulation of casein looks like this:

$$\left\lceil \begin{array}{l} \text{Caseinate Ca} \\ \qquad\qquad\quad \\ \text{Phosphate Ca} \end{array} \right. + HR \rightarrow [\text{casein}] + Ca(H_2PO_4) + CaR$$

The basic diagram of obtaining milk protein by acid coagulation is presented in Figure 2.4.

The rennet coagulation. Its mechanism has not been completely researched yet. Different theories exist. There are two stages of rennet coagulation: fermentation and coagulation stages.

One of the theories is the phosphoamidase theory [2]. It postulates that there are two stages of rennet action. At the first - “fermentation” - stage casein transforms into paracasein. At the second - “coagulation” - stage paracasein forms a clot. The first stage of rennet coagulation is led by rennet, and the second stage - by ions of calcium.

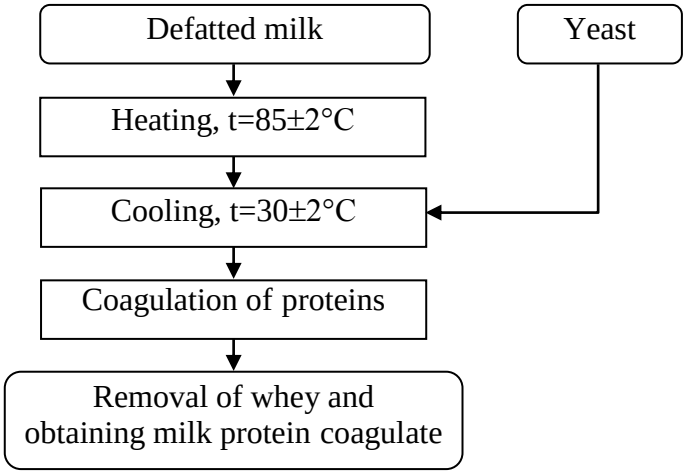

Figure 2.4 Basic flowchart of obtaining milk protein by acid coagulation.

Owing to breaking phosphoamide bond, OH-groups of phosphorus acid interact with bivalent ions of metals, and ions of calcium react with two OH-groups forming calcium “bridges” between protein particles. As they grow, the milk clot forms.

Proteolytic action of rennet is the base of another theory called hydrolytic. K.K. Gorbatova believes that at the first - fermentation – stage chemosin splits peptide bond between phenylalanine and methionine in polypeptide chains of χ-casein [5, 9]. As a result, the χ-casein molecules break down into para-χ-casein and glycomacropeptide, which causes the colloidal system’s stability to decrease.

At the second – coagulation – stage paracasein micelles, which are partially destabilized by rennet, assemble in aggregates, then in chains, which form a space net, i.e. gel-forming takes place.

The process of rennet coagulation of casein, as well as the process of acid coagulation is divided into four stages: the first is the induction method, which comprises the fermentation stage and the stage of latent coagulation; the second is the mass (manifest) coagulation stage; the third is the net forming and clot compression stage; the fourth is the sineresis stage.

Whey proteins do not coagulate under action of rennet, they are removed with whey during sineresis [3, 6, 10].

Figure 2.5 shows the flowchart of obtaining milk protein by rennet coagulation.

The rennet-acid coagulation. A combined technique of milk protein coagulation called the rennet-acid method is used to manufacture milk protein products, for example curd and soft cheeses. In this case, proteins are obtained by both rennet and lactic acid, which accumulates during lactic acid fermentation.

The combined action of rennet preparation and lactic acid on casein makes the coagulation process 2-4 shorter. It is due to the fact that casein transforming into paracasein shifts isoelectric point from pH 4.6 to 5.2.

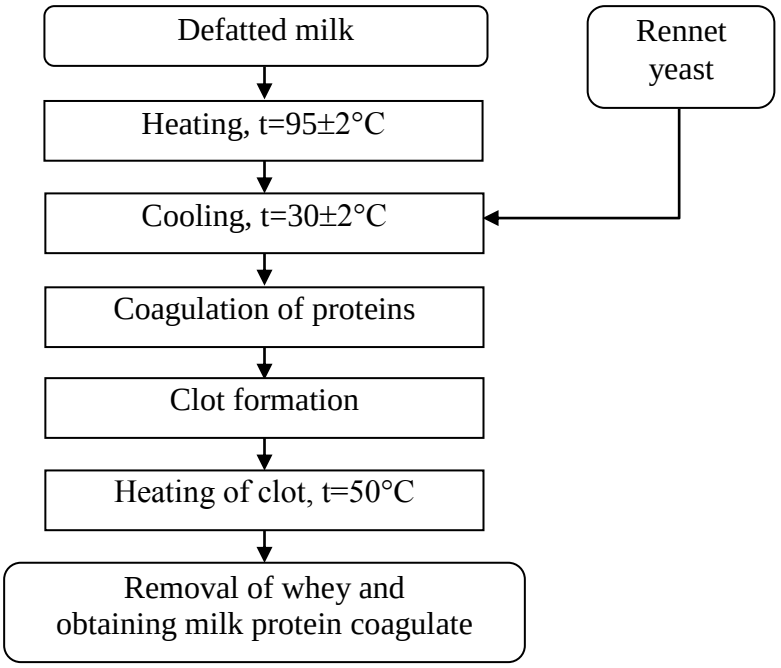

Figure 2.5 Basic flowchart of obtaining milk protein by rennet coagulation.

Thus, the clot forms faster than during acid coagulation and has a stronger structure. Sineresis and dehydration go faster in these clots, which is necessary for production of such milk proteins as curd and soft consistency cheeses [34, 35]. Figure 2.6 shows the diagram of obtaining milk protein by rennet-acid coagulation.

The thermocalcium coagulation. The theoretical foundations of obtaining milk protein (coprecipitate) from milk by high temperature and calcium chloride were first worked out in 1953 by Prof. P. F. Diachenko, I.N. Vlodavets and E.A. Bogomolova [2].

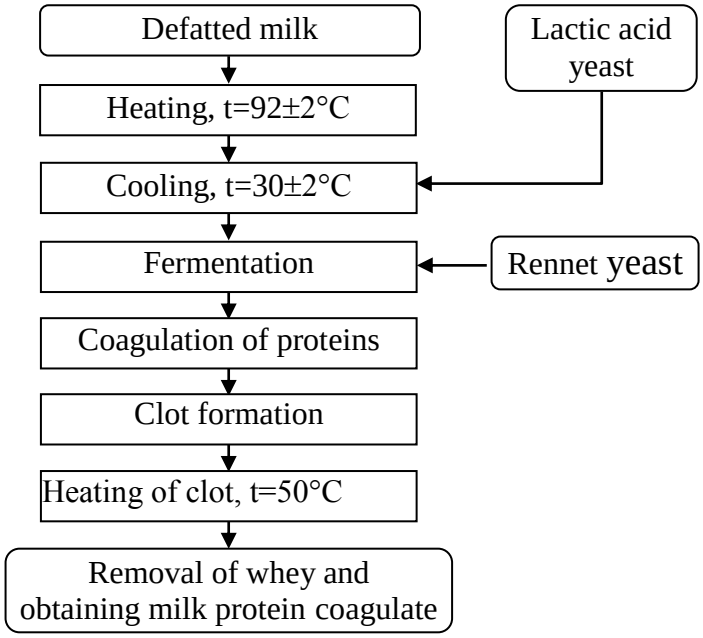

Figure 2.6 Basic flowchart of obtaining milk protein by rennet-acid coagulation.

P. F. Diachenko described the non-stop process of obtaining calcium precipitate in 1957. The mechanism of calcium's action is in lowering the protein particles' negative charge due to its joining the negatively charged groups. As a result, the electrically neutral particles of casein aggregate with the help of calcium ions and precipitate. The thermocalcium coagulation may be shown as follows:

$$2\,[\,\text{Caseinate} - \text{Ca} - \text{phospate}]\,H^{+} + CaCI \longrightarrow$$
$$\longrightarrow\,[\,\text{Caseinate} - \text{Ca} - \text{phosphate}]\,Ca^{++} + 2HCI$$

The essence of this process is described in Chapter 1.

It is known that calcium-phosphate-casein complex is highly resistant to milk heating. It was found that there is a direct relationship between the temperature of milk heating and the amount of calcium chloride necessary for the irreversible coagulation of casein particles: the higher the temperature, the less calcium chloride spent for coagulation. Thus, for casein precipitation at 65°C the necessary concentration of calcium chloride is about 3 g/l, at 85°C – 1.1 g/l, and at 95°C – 0.97 g/l.

The research has established that it is enough to raise calcium chloride concentration in milk to 0.12…0.15% at 85°C to cause instant protein coagulation in fresh defatted milk with acidity 18°T [1, 2, 6].

Taking into consideration the uncontestable effectiveness of obtaining milk proteins by calcium chloride at high temperatures, this method was named

thermocalcium. Figure 2.7 shows the diagram of obtaining milk protein by thermocalcium coagulation.

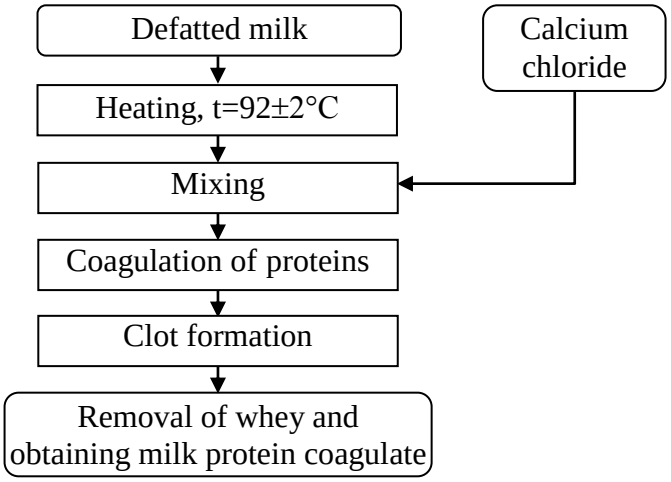

Figure 2.7 Basic flowchart of obtaining milk protein by thermocalcium coagulation.

A distinct feature of the proposed method of calcium coagulation is great protein output due to the precipitation of not only casein, but also whey proteins.

As soon as the temperature reaches 75°C, whey proteins denaturation and aggregation begins, though their globules' size is many times smaller than the size of casein globules. However, they also grow due to assembling. It happens because of the interaction of denatured whey proteins with casein during heating of defatted milk up to 90-95°C. Casein flocculus, which formed during the thermocalcium coagulation, capture whey protein particles. The protein obtained in this manner comprises not only casein particles, but also contains whey proteins and is called coprecipite, i.e. precipitated.

It has been established that at 75°C the degree of whey proteins utilization during the thermocalcium coagulation is 24%, at 85°C it is 78%, and 95°C – 100%. Because of this the biological value of milk protein products obtained on the base of the thermocalcium coagulation rises substantially, since the amino acid composition of whey proteins with essential deficient amino acids is better than the amino acid composition of casein. However, recently the thermocalcium coagulation of milk proteins has been less used, because the obtained product has metallic smack, which considerably narrows its field of application.

This is the reason why the thermoacid coagulation of milk proteins free of this consequence is of essential interest at present.

The thermoacid coagulation. The comprehensive and complex obtaining of milk proteins can be performed by the thermoacid coagulation as well. Like the

thermocalcium coagulation it has two stages. The method is described in detail in Chapter 1. Figure 2.8 shows the diagram of obtaining milk protein by thermoacid coagulation.

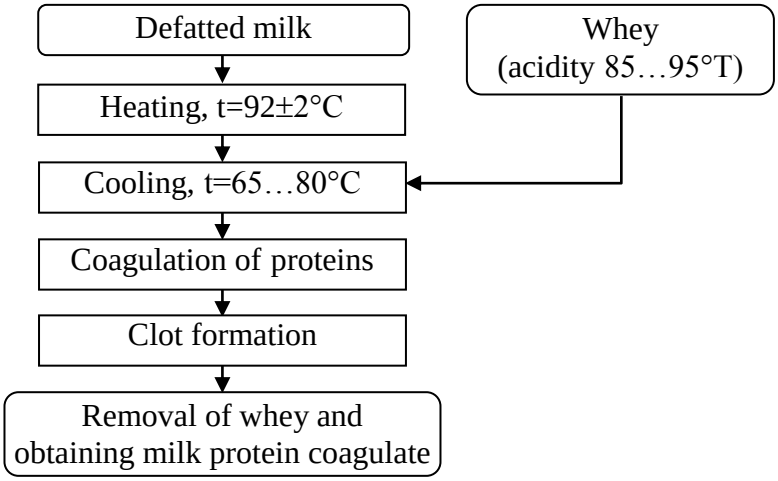

Figure 2.8 Basic flowchart of obtaining milk protein by thermoacid coagulation.

The obtained precipitate is characterized by neutral, slight milk flavor and scent. It is of white color, and elastic, resilient consistency.

This method of protein precipitation is comprehensively complex, which substantially raises the degree of utilization of milk proteins substances [1, 6].

Owing to its effectiveness, it finds massive practical application because it has a number of advantages over other milk protein production methods.

During the usual acid milk protein coagulation only casein transfers to a clot, while whey proteins remain in whey, which lowers the nutritional and biological value of milk protein products. And since the biological value of whey proteins is higher compared to casein, once again it confirms the necessity of their obtaining from whey and their use in food production.

2.2 The Technology of Obtaining Milk Protein by the Thermoacid Method.

A well-known technique of thermoacid coagulation comprises the heating of defatted milk up to 91…95°C, precipitation of milk proteins by milk cultures yeast or acid curd whey, obtaining and slight pressing of protein mass [1, 6].

It is known that the strucrural-mechanical and syneretic properties of milk protein clots are considerably dependent on the thermal treatment of milk [5, 17]. The higher the temperature and the longer its effect during the structure forming of milk protein clots, the more intensive is the sineresis process, the more intensively

“shrinks” a clot due to pressing out moisture, and the denser and harder becomes its consistency.

It is probably the reason for the traditional thermoacid method’s drawback, which is the output milk protein coagulate’s dry, dense and very often grainy consistency. It may be explained by the fact that the exposure of protein globules to lactic acid for a comparatively long time at 91…95°C accelerates gel sineresis, i.e. pressing the moisture out of milk protein mass’s capillaries. The milk’s exposure to high temperatures of 91…95°C is accompanied by the denaturation of whey proteins. When heated milk is mixed with acid curd whey, they aggregate with casein, and the denatured casein and whey proteins complex is produced with the release of moisture [10]. The clot’s structural-mechanical properties are formed. The further exposure to high temperatures causes the decrease in the clot’s volume, mass, plasticity, and the increases in its mechanical strength and elasticity.

To improve the quality and consistency of milk protein obtained by thermoacid coagulation with the aim of its wider use in the technologies of culinary and confectionary products with uniform, smooth, tender, grainless structure and consistency we proposed to shorten the high temperature exposure at the stage when structural-mechanical properties form. After heating up to 91…95°C milk was cooled down to 65…80°C. Then curd whey was added for protein substances coagulation.

The lowering of the milk’s temperature from 91…95°C, at which whey proteins denature and later separate together with whey casein during coagulation, to 65…80°C lets obtain protein mass with a more tender consistency, which can be easily spread.

Table 2.3 presents the organoleptic evaluation of the obtained milk protein’s quality.

The analysis of the experimental data (Table 2.3) lets draw conclusions about the quality of the milk protein, whose rational texture indices have been obtained when mixing milk at 65…80°C and whey.

Thus, the temperature (65…80°C) of mixing milk and whey is determined by the fact that a higher temperature and a longer exposure contributes to a more intensive pressing of moisture out of a clot, and so, soft, plastic, easily spread mass is unattainable. Further processing of such protein is made more difficult by its compressed consistency. The resulting milk protein mass is difficult to spread.

When the mixing temperature is lower, the dehydration of a clot decreases considerably, and the output product has the consistency close to liquid. It is mixed with whey, which is difficult to separate.

Table 2.3 – The experimental evaluation of "The Method of Obtaining Milk Proteins"

Indices	Traditional method	Temperature of milk before mixing with whey				
		85°C	80°C	75°C	65°C	55°C
Consistency	Too dense, dry, grainy	Too dense, flexible, elastic	Softer, more flexible, easily spread	Soft, tender, flexible, uniform	Very tender, spreading, paste-like	Close to liquid-like, too moist, with whey difficult to separate
Color	White	The same	The same	The same	The same	The same
Flavor	Characteristic of milk products	The same	The same	The same	The same	The same
Aroma	Characteristic of milk products	The same	The same	The same	The same	The same
Organoleptic evaluation of quality, points	3.8±0.2	4.2±0.2	5.0±0.0	5.0±0.0	5.0±0.0	3.8±0.2

The product obtained at 75±2°C has better attributes.

The analysis of the data obtained during the research of the structural-mechanical properties of coagulates shows that they may be largely controlled and adjusted (Figure 2.9).

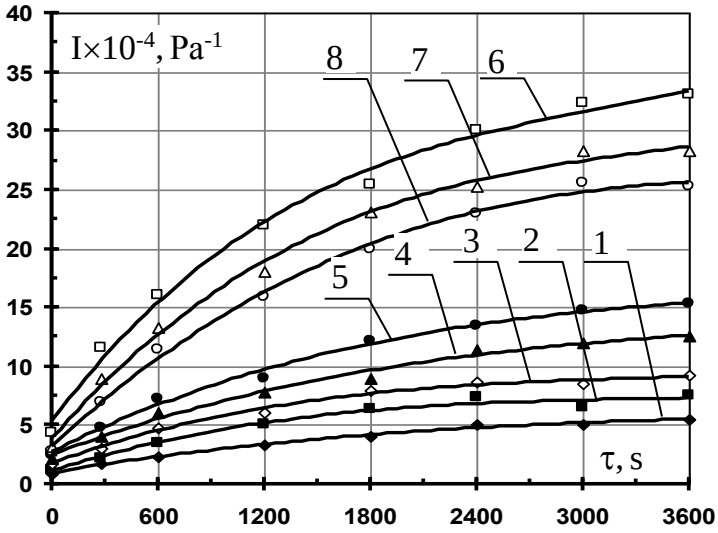

Figure 2.9 Compliance I=$f(\tau)$ of milk protein: 1,3 – traditional technology, not rubbed (I) and traditional technology, rubbed into pulp (3); 2,4,5,6,8 – newly-developed technology of mixing milk at 85, 80, 75, 65 i 55°C respectively with whey; 7 – curd cheese mass

The diagram (Figure 2.9) shows the flexibility curves for milk protein, obtained in different temperature modes of coagulation. The study of the structural-mechanical properties kinetics let us show that the milk protein obtained by mixing milk at 80°C and whey (curve 4) has the flexibility value $I = 12.05 \times 10^{-4}$ Pa^{-1}. It is close in its structural-mechanical properties to the milk protein rubbed into pulp (curve 3), which was obtained by the traditional method during high-temperature coagulation. It leads to a conclusion that rubbing may be omitted. However, the milk protein with the structural-mechanical properties similar to those of the milk protein rubbed into pulp can be obtained.

The milk protein obtained by mixing milk at 65°C and whey (curve 6) has the flexibility value $I = 27.76 \times 10^{-4}$ Pa^{-1}. It is close in its structural-mechanical properties to the curd cheese mass (curve 7). The curd cheese mass gains plasticity due to the mechanical mixing in the presence of sucrose [13], and the milk protein gains plasticity due to the increase in the volume of disperse environment.

The analysis of the structural-mechanical and organoleptic researches has shown that when milk is cooled down to 85 °C, the output product has a flexible-elastic consistency, and the highest coefficient of elasticity 13.7 10^2Pa (curve 2) in Figure 2.9. The relative plasticity is 45%, the relative elasticity is 21% (Figure 2.10).

The coefficient of elasticity of the other sample is 1.7 times lower than that of the former (Figure 2.9, 4). The relative plasticity grows by 8% and reaches 53%. The relative elasticity is 19%. The coefficient of elasticity of Sample 3 is 1.3 times lower than the previous one. The relative plasticity grows and reaches 6% (Figure 2.10). The relative elasticity falls to 17%. Thus, the product may be characterized as plastic (Figure 2.9, 5).

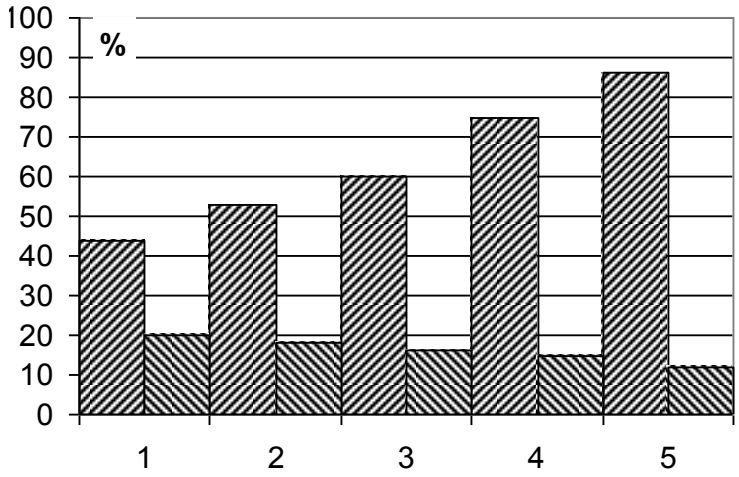

Figure 2.10 The relative elasticity – ▨ and relative plasticity - ▨ of milk protein obtained by mixing whey and milk at, °C: 1, 2, 3, 4, 5 - 85, 80, 75, 65 and 55 respectively

The character of curves 4, 5, 6 shows considerable fluidity of the researched systems. At the same time the obtained protein was characterized by plasticity and good molding.

Thus, the research of the structural-mechanical properties has established that the technological process of milk protein coagulate production in the chosen temperature range allows to change the coefficient of elasticity from 8.3×10^2Pa to 3.6×10^2Pa. In this case the relative plasticity of the product grows from 53 to 75%, and its relative elasticity decreases from 19 to 16%.

The research has helped establish that the diminished exposure to high temperatures at the stage of the formation of a clot's structural-mechanical properties cause the system's flexibility to increase, and the elastic properties to decrease. The system acquires plastic attributes. The rational technological parameters were chosen in the variability interval limited by the technological parameters of the rubbed milk protein mass on the one hand, and of the curd cheese mass on the other hand.

The development of the technology of obtaining milk protein is performed on the base of the analysis of the literary data on the correlation of the amount of the output raw materials taking into consideration the output components' properties, the selection of the rational temperature modes and the determination of the specific features of the technological process.

The aim of selecting the rational technological pattern is the improvement of the structural-mechanical properties of milk protein for manufacturing products from milk protein mass with various nutritional additions. The properties of prospective added ingredients were taken into consideration to lower the cost process preparation of raw materials.

The different authors' research of the effects of different milk proteins thermocoagulation modes on organoleptic, physical-chemical, structural-mechanical properties and milk protein output allowed to determine the quantitative ratios of output components for the previous experiment, conditions and agents, which influence the dehydration process, the completeness of precipitation (the temperature of heating of basic raw material, duration of holding for forming a clot, duration of pressing out whey).

The best quality of milk protein may be attained by use of 25…35% of whey with acidity 95…120°T and temperature 20°C [14].

The choice of 95…120°T acidity of whey in this work is determined by the fact that after a clot separation it has low acidity of 50…60°T [15], and a comparatively long time period is necessary to accumulate lactic acid to reach

higher acidity. At such acidity the volume of whey added was 30% of coagulation mixture. It is not reasonable to add more than 25…35% of whey, because it decreases the amount of milk, which leads to diminished output, increased loss of dry matter, harder consistency. Holding during 5 minutes ensures maximal completeness of precipitation [16].

Figure 2.11 shows the basic diagram of milk protein production.

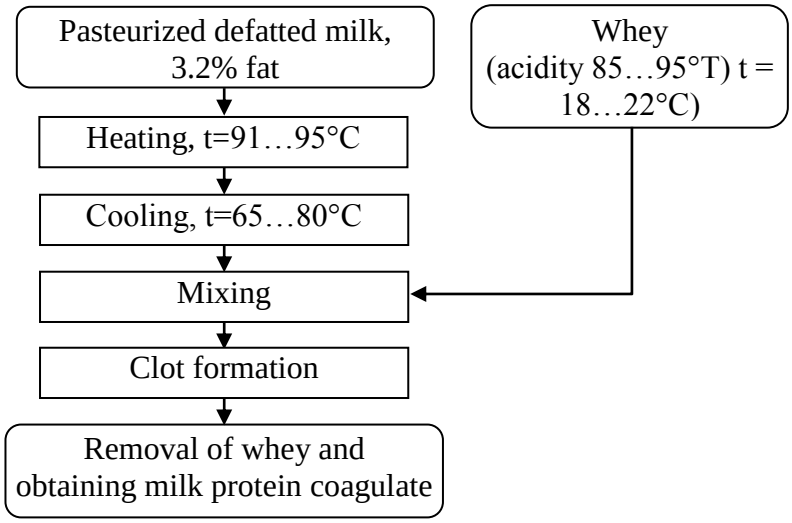

Figure 2.11 The basic diagram of milk protein production.

Taking into consideration all factors, parameters and properties of milk protein obtained by the improved method of thermoacid coagulation the technology of obtaining milk protein based on the change of coagulation temperature modes has been developed. It comprises the heating of milk up to 91…95°C, the cooling down to 65…80°C, mixing with whey, which is 30% of the volume of the coagulation mixture, with acidity 85…95°T and temperature 18…22°C. The process of mixing was stopped after coagulation floccules of protein appeared at the liquid stage. The protein clot was held for (5...10)×60 sec for fixaing, then separated by self-pressing. The obtained coagulate from milk with 3.2…3.5% fat is characterized by not more than 70% moisture; from defatted milk – not more than 80%.

2.3 The Technological Properties of Milk Protein Obtained by Thermoacid Method

The analysis of the technologies of products from milk protein has shown that their rubbing, further pressing to the necessary mass portion of moisture, plasticization and mixing with recipe ingredients are usual integral parts of their processing schemes [11, 15, 17, 18, 19].

The study of the structural-mechanical properties of milk proteins obtained by the new technology has established that it is possible to obtain a milk protein mass with desired structural-mechanical properties (Figure 2.9, 2.10). The correlation between the organoleptic, physical-chemical, structural-mechanical indices and their effect on a product's technological properties and quality has been found.

Table 2.4. shows the results of physical-chemical researches of milk proteins obtained in different temperature modes.

The data presented in Table 2.4 show that the temperature of the coagulation process affects the milk protein output, acidity and fat content.

Table 2.4 – The physical-chemical indices of milk proteins

Temperature of cooling of milk, °C	Physical-chemical indices			
	Protein mass output, % of milk mass	Acidity, °T	Moisture, %	Fat content, %
85	12.9	88	63.5	15.8
80	14.1	90	64.8	15.3
75	14.3	91	65.8	15.0
65	14.7	93	67.6	13.8
55	19.4	96	74.2	10.8

The milk proteins obtained by mixing milk at 85°C and whey have the lowest moisture-retaining capability and thus, the lowest moisture content of 63.5% due to a prolonged exposure of milk globules to lactic acid at high temperature.

When the milk's temperature is lowered from 85°C to 65°C, the milk protein output grows because of the unpressed-out moisture, which is witnessed by the increase in moisture content from 63.5 to 67.6%. The most important changes in the output and moisture content are observed at more than 80°C and lower than 65°C. When the temperature of the process is 55°C, the milk protein output grows considerably and reaches 19.4% of milk mass. However, in this case the milk protein has insufficient organoleptic indices and very high moisture content of 74.2%.

When the milk's temperature is lowered during coagulation, the fat content decreases. The product obtained at milk's temperature 55°C before mixing it with whey has the lowest fat content.

Its fat content is 10.8%. The fat content of the milk protein obtained in the chosen temperature interval is 15.3…13.8%. The milk protein obtained at 75±2°C has been chosen for culinary production because of its organoleptic and physical-

chemical indices. It has a soft, tender, flexible, uniform consistency. Its output is 14.3% of milk mass with 65.6% moisture, 15.0% fat, and 91°T acidity.

This way the research has established that at lower processing temperatures (in the interval of 55…85°C) the final product's fat content is lower and its output is higher due to pressing the moisture out of the milk protein coagulate. So, the volume concentration of the disperse stage has been chosen as an objective index affecting consistency.

Fat's positive effect on milk protein clot's consistency is well-known. At the same time the study of the kinetics of physical-chemical indices, notably the volume concentration of the disperse phase and the accompanying change in correlation between the disperse phase and product's internal environment (Table 2.5), which characterize the extent of hydration, let establish that it is them that seriously affect the product's technological properties.

Table 2.5 – The technological properties of milk protein obtained in different temperature modes of coagulation

Temperature of cooling of milk, °C	Content of disperse environment, g/100g	Content of disperse phase, g/100g	Volume concentration of disperse phase, m^3/m^3	Viscosity, $\eta \times 10^6$ Pa·s	shear deformation, $(\gamma_2-\gamma_1)\times 10^{-2}$
85	63.5	36.5	0.287	7.50	7.20
80	64.8	35.2	0.275	5.10	7.28
75	65.8	34.2	0.267	3.42	10.80
65	67.6	32.4	0.251	2.16	16.12
55	74.2	25.8	0.195	1.72	17.56

The hydration of milk protein particles is determined by the presence of polar groups in protein molecules. During absorption water dipoles place themselves in several layers around the protein molecule's hydrophilic centers forming a hydrate capsule. The first layer of the capsule has the strongest bond with the protein, the next layer has lower bond energy. The properties of water of the first layer are closer to bound, the properties of water of other layers are closer to the properties of free water [5].

Water with solute substances functions as disperse environment, through whose interlayers the particles and molecules interact, which takes place during the formation of coagulation structures of disperse systems of suspension type, milk protein being the one.

At the greatest compression level of the structure caused by dehydration due to long high temperature exposure at the stage of formation of a clot's structural-

mechanical properties the liquid environment interlayers' thickness is minimal and the interaction between the particles is maximal. This leads to formation of large coagulates and dense of areas, which is the cause for dense consistency and graininess [20, 21].

The thickness of a layer depends considerably on the content of disperse environment. Thus, the increase of a product's moisture content depends on the increase of the free water content.

As we can see in Table 2.5, when the milk's temperature is lowered from 85°C to 55°C before mixing it with whey, the disperse environment content increases by 17%. The shear property values also grow, and the system transforms from hard-type to liquid-type, which is confirmed by the results of rheogoniometry and organoleptic indices (Table 2.3, 2.5).

In the researched temperature interval of 85°C…55°C the volume concentration of the disperse phase decreases from 0.287 to 0.195 $м^3/м^3$, which causes the diminishing of contacts between particles in a unit of volume and contributes to lowering the mechanical strength of the structure. The changes in viscosity and shear deformation are determining factors in the process of forming. When the product is dehydrated and the volume concentration of the disperse phase is increased (Table 2.5), viscosity increases and shear deformation decreases. When the milk's temperature lowers from 85°C to 55°C during coagulation, the system's viscosity increases 1.5 times.

Shear deformation (Figure 2.12) in the structure develops comparatively weakly and reaches 7.28 at (60×60) sec. At 75°C viscosity decreases 2 times compared to the first sample, and shear deformation increases 1.5 times.

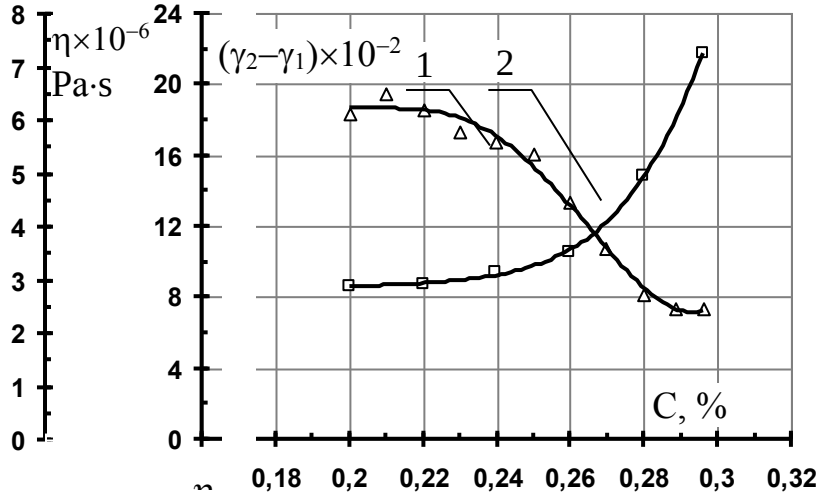

Figure 2.12 The dependence of: shear deformation ($\gamma_1 - \gamma_2$) (1) and viscosity ŋ (2) of milk protein on volume concentration of the disperse phase V_{dph} when mixing milk with temperatures, ^{0}C: 1, 2, 3, 4, 5 - 55, 65, 75, 80, and 85 respectively and whey.

The investigation of the kinetics of viscosity and shear deformation has shown that in the researched temperature interval their substantial changes are observed (Figure 2.12). Viscosity lowers from 5.10×10^{6}Pa·s to 2.16×10^{6}Pa·s, shear deformation increases from 7.28×10^{-2} to 16.12×10^{-2}. Beyond the chosen interval the indices change insignificantly.

As Table 2.5 and Figure 2.12 show, the rational parameters in the 80…65^{0}C temperature interval are: viscosity $(2.16...5.10)\times10^{6}$ Pa·s, shear deformation $(7.28...16.12)\ 10^{-2}$, volume concentration of the disperse phase 0.275...0.251 m^3/m^3.

Thus, the investigation of the milk protein's structural-mechanical properties has shown that the increase of free moisture content contributes to weakening the bonds between protein molecules, which gives protein plasticity.

The improvement of technological properties of milk protein is possibly determined by the augmentation of interlayers of liquid environment, which impede the particles approaching each other and provide for mobility of certain elements of the structure. The milk protein's technological properties (forming, easy mobility) depend on the duration and intensity of mechanical exposure, which is confirmed by the results of the research.

It has been established that the dispersion degree, i.e. the dominant size of particles, affects the milk protein's state, its structural-mechanical properties even at constant phase concentration (Table 2.6). The measurements of the average diameter of the particles have shown that the initial sizes of the particles of the milk protein obtained by the newly-developed technology are a little larger than the size of the particles of the rubbed protein obtained by the traditional technology. The particles' sizes decrease during mixing. The longer is mixing, the smaller become the particles.

Table 2.6 – Changes of particles dispersion and milk protein's structural-mechanical properties during mechanical exposure

Product name and type of mechanical exposure	Volume concentration of disperse phase, m^3/m^3	Duration of mechanical exposure, s	Diamenter of particles, $d_{avarage}$ $\times10^{-}6$, m	Degree of concentration, units.
Protein obtained by the traditional technology				
Rubbing	0.290		87±10	210±10
Protein obtained by the newly-developed technology				
Mixing	0.267	180	110±9	189±5
	0.267	300	92±7	202±7
	0.267	420	65±9	215±6
	0.267	600	63±9	218±8

As Table 2.6 shows during mixing lasting from (3×60) to (10×60) seconds the particles average diameter changed from (110±9)×10^{-6}m to (68±9)×10^{-6} m at constant volume concentration of disperse phase 0.267 m^3/ m^3 (curve 1 in Figure 2.11). The penetration degree increased by 30 units (curve 2 in Figure 2.11).

As the garphs (Figure 2.13) show the rational parameters are at mixing duration (4-60…7-60) s. In this case the penetration degree is 192…212 units, the particles' average diameter is (77…97)×10^{-6} m, which corresponds to the technological parameters of the milk protein obtained by the traditional technology after rubbing (Table 2.6) (the average size of the particles is (87±10)×10^{-6} m, the penetration degree is 210±10 units, the volume concentration of disperse phase is 0.290 m^3/ m^3).

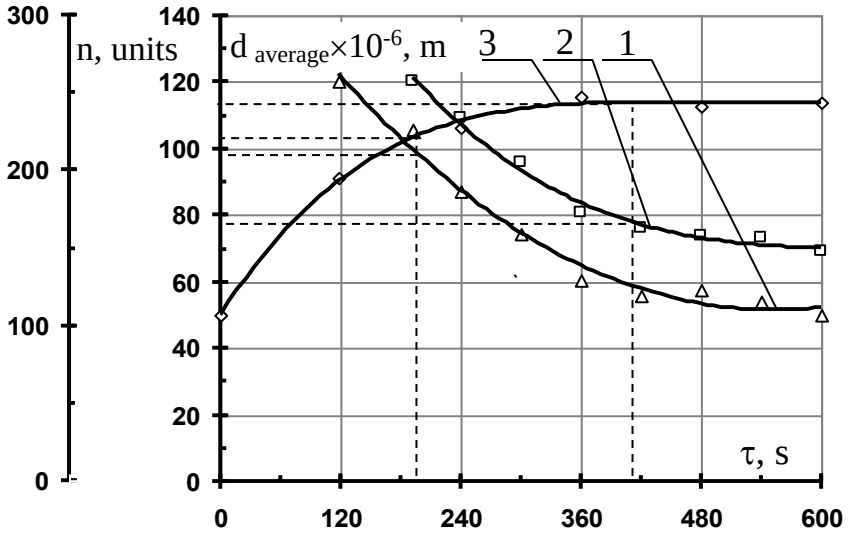

Figure 2.13 Dependence of the average diameter $d_{average}$ of the particles of rubbed milk protein (1) and non-rubbed milk protein (2) and the penetration degree n (3) of the milk protein obtained by the newly-developed technology on the duration of mixing at volume concentration of disperse phase 0.267 m^3/m^3

The curves confirm that it is at this duration of mixing that the considerable changes in dispersity and structural-mechanical properties of the milk protein mass are observed. Further mixing is not productive.

2.4 The Estimation of the Nutritional and Biological Value of Milk Protein

The above experiments (Chapters 2.2, 2.3) let us choose among the researched matter the most rational in its consistency, structural-mechanical, organoleptic and physical-chemical indices variant of milk protein for further use in culinary products manufacture.

Because the method of obtaining milk protein makes possible to produce a new quality product with a distinct fat and moisture content, it is necessary to investigate its quality indices.

The chemical composition characteristics. The comparison of the chemical composition of the milk protein obtained by the newly-developed and traditional technologies with the semi-fatty milk protein obtained by the traditional technology and fatty curd [22, 23].

Table 2.7 shows the research data on the chemical composition.

The analysis of the data in Table 2.7 has shown that the solids content in fatty milk is only slightly different from the one in fatty lactic acid curd. However, the protein percentage in fatty milk protein's solid is 9.2…9.9% higher than in fatty lactic acid curd, which indicates its higher nutritional value. Fatty milk protein contains 9.0…9.7% less protein in solid than semi-fatty, however, its fat content is 10.1…10.4% higher. Taking into consideration that fat of milk contains valuable substances, fat-soluble vitamins included, we may assume that the nutritional value does not diminish. In addition, the protein-fat ratio in fatty milk protein is 1:(0.92...0.94), which is close to rational. The same cannot be said about the semi-fat milk protein (1:0.6), and even less so about defatted (1:0).

Table 2.7 – The chemical composition of milk protein

Product name	Solids, g/%	Proteins		Fats		Carbohydrates	
		g/%	% in solids	g/%	% in solids	g/%	% in solids
Newly-developed technology fatty milk protein	34.0±1.2	16.3±0.8	47.9±2.4	15.0±0.4	44.1±1.2	1.0±0.1	3.0±0.3
Traditional technology fatty milk protein	37.1±1.0	17.5±0.5	47.2±1.3	16.5±0.6	44.4±1.6	1.1±0.1	3.0±0.3
Traditional technology semi-fatty milk protein	32.3±1.0	18.4±0.5	56.9±1.3	11.0±0.6	34.0±1.6	0.9±0.1	2.8±0.3
Fatty lactic acid curd	30.8±1.0	14.0±0.5	38.0±1.3	18.0±0.6	48.9±1.6	2.9±0.1	7.9±0.3

The amino acid and fractional composition of milk proteins. The fatty milk protein is not limited in essential amino acid content (Table 2.8), confirms its assumed full value. In addition to casein it contains whey proteins, whose percentage in solid is 5…7% (Table 2.8). Fatty lactic acid curd contains only casein and no whey proteins.

Table 2.8 – The fractional composition of milk protein

Name	Casein, %			Serum proteins, %		
	of total protein	in 100 g of product	in solid	of total protein	in 100 g of product	in solid
Newly-developed technology fatty milk protein	85.3±0.3	13.8±0.5	40.8±1.4	13.1±0.5	2.1±0.2	6.2±0.6
Traditional technology fatty milk protein	84.9±0.4	14.9±0.6	40.1±1.6	13.8±0.5	2.4±0.1	6.5±0.6

Thus, the analysis has shown that, despite a lower protein content in fatty milk protein compared to semi-fatty and defatted milk protein, it is fully valuable, which confirms its high nutritional value.

The casein and whey proteins contents in the fatty milk protein obtained by the newly-developed technology and in the traditional technology fatty milk protein are virtually similar.

Probably, it may be explained from the chemical point of view by the fact that during heating of milk in both cases there is denaturation of whey proteins, which later precipitate combined with casein. Obviously, the further lowering of the coagulation temperature does not considerably affect the degree of whey proteins precipitation. The whey protein content in the researched samples is (13…14)% in both cases. Table 2.9 shows the amino acid composition of milk protein.

Table 2.9 – The amino acid composition of milk protein

Amino acid	Traditional technology fatty milk protein		Newly-developed technology fatty milk protein		Fatty lactic acid curd	
1	2		3		4	
	g/100 g	% in solid	g/100 g	% in solid	g/100 g	% in solid
Essential amino acids						
Total:	7.319	19.7	6.674	1.6	5.832	15.8

1	2		3		4	
Valine	1.190	3.2	1.075	3.2	0.838	2.3
Isoleucine	1.070	2.9	0.960	2.8	0.690	1.9
Leucine	1.476	4,0	1.380	4.1	1.282	3.5
Lysine	0.987	2.0	0.906	2.7	1.008	2.7
Methionine	0.556	1.5	0.501	1.5	0.384	1.0
Threonine	0.945	2.5	0.870	2.6	0.649	1.8
Phenylalanine	1.095	2.9	0.982	2.9	0.762	2.1
Replaceable amino acids						
Total:	9.908	26.7	9.384	27.6	8.115	22.1
Alanine	0.741	2.0	0.674	2.0	0.428	1.2
Arginine	0.542	1.5	0.511	1.5	0.579	1.6
Asparaginic acid	1.185	3.2	1.068	3.1	0.924	3.6
Histidine	0.523	1.4	0.511	1.5	0.447	1.2
Glycine	0.409	1.0	0.379	1.1	0.258	0.7
Glutaminic acid	3.335	9.0	3.185	9.4	2.457	6.7
Proline	1.015	2.7	1.976	2.9	1.310	2.5
Serine	1.024	2.8	1.096	3.2	0.789	2.1
Tyrosine	1.070	2.9	0.924	2.7	0.875	2.4
Cystine	0.064	0.2	0.060	0.2	0.048	0.1

Compared to other fats milk fat has a high content of them. The biologically important polyunsaturetated fatty acids (linoleic and linolenic acid) amount to 6.5…7% in milk protein, which is much less compared to vegetable oils (sunflower oil – 57.6; soy oil – 61.2; cottonseed oil – 50.8). Their low content is taken into consideration when culinary products and dish recipes are worked out on their base. Table 2.10 shows the amino acid score of the fatty milk protein.

Table 2.10 – The amino acid score of the fatty milk protein

Amino acid	Level recommended FAO/WHO		Newly-developed technology fatty milk protein		Traditional technology fatty milk protein	
	mg 1 g of ideal protein	% of scale	mg	%	mg	%
Lysine	55	100	55.6	101.1	56.4	102.5
Valine	50	100	67.8	135.6	68.0	136.0
Isoleucine	40	100	58.9	147.2	61.1	152.9
Leucine	70	100	84.7	120.9	84.3	120.5
Phenylalanine + Tyrosine	60	100	116.9	194.8	123.7	206.2
Threonine	40	100	53.4	133.4	54.0	135.0
Methionine + Cystine	35	100	34.4	80.4	35.42	101.1

Taking into consideration the biological functions performed by fatty acids in human organism, the use of the fatty milk protein has advantages over the semi-fatty milk protein, in which there are much few fatty acids, even more so over the defatted milk protein, where fatty acids are virtually absent.

The comparison of fatty acid composition of milk protein obtained by the newly-developed and traditional technology has shown that the lowering of the coagulation temperature has almost no effect on the fatty acid content in their fluctuation range in milk fat and in the method's accuracy limits.

Table 2.11 shows the milk protein's fatty acid composition of lipids.

Table 2.11 – The fatty acid composition of lipids in milk protein (content percentage of mass)

Amino acid	Milk fat [13]	Newly-developed technology fatty milk protein	Traditional technology fatty milk protein
Saturated	40.4…84.4	57.63	57.90
$C_{8:0}$ (caprylic)	0.4…1.7	3.01	3.57
$C_{10:0}$ (capric)	0.8…3.6	1.34	1.85
$C_{12:0}$ (lauric)	0.8…3.9	3.33	3.88
$C_{14:0}$ (myristinic)	7.6…13.2	9.75	8.17
$C_{14:0}$ (isomyristinic)	-	0.74	0.93
$C_{15:0}$ (pentadecanoic)	0.8…1.5	1.78	1.86
$C_{16:0}$ (palmitic)	20.0…36.0	27.00	23.90
$C_{16:0}$ (isopalmitic)	-	0.99	1.13
$C_{17:0}$ (margarine)	0.7…1.0	0.53	0.31
$C_{18:0}$ (stearic)	5.5…13.7	9.16	10.83
Unsaturated, including: monosaturated:	21.2…55.7	42.37	42.10
$C_{10:1}$ (caproleic)	0.1…0.4	0.98	1.65
$C_{12:1}$ (lauric)	0.2…0.4	0.78	1.10
$C_{14:1}$ (myristoleic)	1.5…3.5	1.77	1.59
$C_{16:1}$ (palmitoleic)	1.5…5.6	4.00	2.87
$C_{17:1}$	-	0.31	1.18
$C_{18:1}$ (oleic)	16.1…37.6	28.19	26.78
Plolyunsaturated:			
$C_{18:2}$ (linoleic)	1.0…5.2	4.43	3.80
$C_{18:3}$ (linolenic)	0.1…2.1	1.91	3.13

The characteristics of mineral composition. The sol part of the fatty milk protein is represented by a wide range of mineral elements. Macro- and microelements of various importance have been found and their qualitative values have been determined (Table 2.12).

Table 2.12 – The mineral composition of milk protein (% of solid)

Mineral elements	Newly-developed technology fatty milk protein	Traditional technology fatty milk protein
1	2	3
Calcium	10.0	10.0
Magnesium	2.0	2.0
Sodium	0.5	0.5
Phosphorus	-20.0	-20.0
Strontium	<0.01	0.01
Iron	0.002	0.002
Manganese	<0.0005	0.0005
Silicon	0.003	0.003
Aluminium	0.003	0.003
Titanium	0.001	0.001
Copper	0.0003	0.0003
Cobalt	<0.0001	0.0001
Nickel	<0.0001	<0.0001
Chromium	<0.001	0.001
Lead	<0.0005	0.0005
Tin	<0.0005	0.0005
Antimony	<0.01	0.01
Barium	0.001	0.001
Boron	0.03	0.03
Berillium	0.0001	0.0001
Arsenic	0.03	0.03
Molybdenum	0.0005	0.0005
Zink	0.005	0.005
Iodine	0.0003	0.0003
Ytterbium	0.0003	0.0003
Cerium	0.01	0.01
Cadmium	0.001	0.001
Zirconium	0.0003	0.0003
Scandium	0.0005	0.0005
Vanadium	0.0003	0.0003
Bismuth	0.0003	0.0003
Gallium	0.0001	0.0001
Indium	0.0005	0.0005
Germanium	0.00005	0.00005
Silver	0.00005	0.00005
Mercury	0.01	0.01

The analysis of qualitative and quantitative composition of mineral elements shows that milk protein is a good source of Ca, Mg, and P, which perform a number of important functions in human organism. The ratio of calcium, phosphorus and manganese in milk protein is (1:2:0.2). This shows that there are more Mg in milk protein than rational balanced diet (1:1.5:0.5) demands [13]. This volume is characteristic of milk and dairy products, e.g. in fermented milk curd (1:1.5:0.15), in fermented milk semi-fatty curd (1:1.4:0.14), in fermented milk fat-free curd (1:1.6:0.2) [9, 10, 11]. Compared to a higher content of Mg, the amount of P is somewhat low. Milk protein has a rather well-represented group of microelements, notably essential Fe, Cu, Mg, Co, I.

One of the quality indices of a final product, which determines harmlessness to organism, is the heavy metal content. Table 2.10 shows that the heavy metal content in food milk protein is within the tolerable limit for the milk and products group [5, 24].

Besides, it is worth mentioning that the lowering of the coagulation temperature in the thermoacid method of obtaining milk protein does not greatly affect the mineral elements content in the developed product.

The vitamin content characteristics. The investigation of the vitamin content has shown that the milk protein from fatty milk contains all fat-soluble vitamins due to the presence of milk fat, which gives it a good advantage over the milk protein from defatted milk.

The comparison of the traditional and newly-developed technology product shows that the conditions of obtaining the latter protein do not affect the fat-soluble vitamins content in the fluctuation limits of the research results, which is confirmed by Table 2.13.

Table 2.13 – The food milk protein's fat-soluble vitamin content

Product	Fat-soluble vitamin content, micromole /g				
	A	D	E	F	K
Newly-developed technology fatty milk protein	0.05±0.01	0.40±0.02	1.00±0.09	3.4±0.2	0.52±0.03
Traditional technology fatty milk protein	0.04±0.01	0.24±0.02	0.89±0.08	3.2±0.2	0.50±0.03

Water-soluble vitamins mostly transfer into whey. Obviously, the diminished dehydration in the proposed method may contribute to keeping in the product the water-soluble vitamins, which stay in whey.

The comparison of the data from Table 2.14 shows that amount of vitamins B1, B2 grows, though insignificantly. The comparison of the quantitative content the water-soluble vitamins in the fatty milk protein has shown that it is especially rich in riboflavin deficient in food products.

Table 2.14 – The content of water-soluble vitamins in food milk protein

Product	Water-soluble vitamins content, mg/%		
	B_1	B_2	PP
Newly-developed technology milk protein	0.35±0.02	0.48±0.01	1.11±0.07
Traditional technology milk protein	0.25±0.02	0.41±0.01	1.38±0.08

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Chapter 3. Working out the Technology of Culinary Products on the Base of the Milk Protein Obtained by the Thermoacid Method

3.1 Working out the recipe composition and processing parameters of curd cake on the base of milk protein

Milk protein obtained by thermoacid method has been used as basic raw material for the curd snacks production (Chapter 2).

The research has shown that milk protein is a unique in its chemical composition and biological value product, which can be used in nutrition as an integral product. Thus, the working out of the culinary products technology using it as an ingredient in their recipes is rational, challenging and promising.

As it has been said before (Chapter 2), while working out the culinary products with the determined organoleptic and physical-chemical properties on the base of milk protein, it is necessary to improve the processing indices and the product's quality. We assume that such additions as apple powder, salt, gelatin and sodium citrate used as ingredients in their recipes may contribute to it.

The said additions contribute to obtaining products, which keep shape well. It is an important factor for the curd snacks production. It lets exclude butter, which is used as a structure forming amendment, from the recipe. The products can be cut and portioned. Their shape remains intact.

Gelatin has been selected as a structure former, because among all known gel-formers it is the cheapest and most available. Another most common structure former is starch. However, because it is of non-protein nature, its use in culinary production on the base of milk proteins can cause certain complications due to the difference in physical-chemical properties. Gelatin's properties, as a protein structure former, allow its use in culinary production on the base of milk proteins without making the technological processing too complicated.

Since recently there has been a trend towards using modified gelatin, sodium citrate has been selected as a modifying addition [1, 2]. When a modifier was being selected, it was taken into consideration that sodium citrate is one of melting salts, which affect protein's structure and change its functional properties.

It is known that sodium citrate changes the system's microstructure, transforms it into melted state increasing its water absorbing capability and swelling capacity [3].

Besides, it impedes the delamination of protein systems, when the temperature rises over the protein coagulation limit. This is important for the technological process, because raising the temperature of the recipe mixture over 65°C causes defects in consistency.

Other modifiers, which change the functional properties as structure formers, are used, i.e. polyatomic alcohols, e.g. glycerol, 0.4% of which is added. They allow to reduce the amount of a structure former spent by 15…25%.

The use of apple powder is of interest, because it enriches a product with valuable nutritional substances. The analysis of the chemical composition shows that apple powder has valuable nutritive properties. It contains 40…70% of sugars, including 25…40% of fructose, 15…20% of glucose, 5…5.5% of pectin, 1.5% of cellulose. In addition, it contains 4…4.2% of protein, 1.5…3% of mineral substances (including Na -114 mg, K – 864 mg, Ca – 80 mg, Mg – 60 mg, P – 76 mg)1.40 mg of vitamins (including C – 12 mg/%, B_1 – 0.02mg/%, B_2 – 0.04mg/%, PP – 0.9 mg/%), tannin and organic acids [4].

Apple powder adds nutritional fibers to the final product, which have a positive effect on human organism. This stresses the use of food fibers in culinary technologies compared to clarified fruit juices, jams and confitures [5, 6]. The Brown colored apple powder can be used as a dye. It adds to the final products' color, gives them a pleasant aroma, and a distinct flavor. When selecting additions for salty curd cakes production, it was noted that additions of small amounts of salt do not significantly raise the concentration of sodium and does not cause any changes in structural-mechanical properties.

The development of the salty curd snacks allows to widen the range of culinary products by creating new dishes in composition with various food products.

When the recipe was developed, it was established that dry gelatin should not be added to the system, because in this case the technological process goes on due to its slow wetting in the system. The preliminary soaking of gelatin accelerates the process. The amount of whey to gelatin was 1:6. While mixing milk protein with sugar and apple powder during (5...7)×60 s the components distribute evenly throughout the mixture (Table 3.1). Sugar dissolves in water, which is present in milk protein. Sucrose distributes evenly throughout. At the same time pectin substances contained in apple powder partially dissolve and swell [7].

After mixing the components the equilibrium mixture was held during (20…30)×60 s to distribute moisture evenly.

It was accompanied by the hydration of high-molecular substances due to free moisture contained in milk protein. The duration of swelling (20…30)×60 s is determined by the necessity to obtain a uniform structure (Table 3.2). Gelatin was soaked in whey and left to swell for (40…60)×60 s. The prepared gelatin was added to the recipe mixture.

Table 3.1 – The correlations of recipe components percentages and processing modes for the sweet curd snack production

Raw materials, modes and processes	Amount, %				
	1	2	3	4	5
Milk protein	87.60	79.95	69.30	61.65	54.00
Gelatin	1.00	1.50	2.00	2.50	3.00
Sugar	3.00	5.00	10.00	12.00	14.00
Apple powder	1.00	3.00	5.00	7.00	9.00
Citric acid	0.90	0.80	0.70	0.60	0.50
Sodium citrate	0.50	0.75	1.00	1.25	1.50
Whey	6.00	9.00	12.00	15.00	18.00
Total	100.00	100.00	100.00	100.00	100.00
Mixing duration, s	180	300	360	420	600
Swelling duration, s	900	1200	1500	1800	2100

Table 3.2 – The experimental evaluation of the sweet curd snack

Indices	Recipe variants				
	1	2	3	4	5
1	2	3	4	5	6
Consistency	does not keep shape, spreading, unmixed clots and undissolved sugar crystals	Curdled, keeps shape, no unmixed clots	Elastic, flexible, uniformly even, curdled	Elastic, flexible, curdled	Dense, resilient, elastic, melted, no curdling felt
Color	Light cream	Light cream	Cream	Light brown	Dark, close to brown
Flavor	Sour milk, not sweet enough, almost untraceable smack of dried apples	Sour milk, tender, sweet with a slight smack of dried apples	Sour milk, tender, sweet with a slight smack of dried apples	Sour milk, tender, sweet with a slight smack of dried apples	Sour milk, very sweet with a distinct smack of dried apples
Aroma	Characteristic of a dairy product	Characteristic of a dairy product	Characteristic of a dairy product	Characteristic of a dairy product	Characteristic of a dairy product
Organoleptic evaluation, points	3.5±0.2	4.6±0.2	5.0±0.1	4.8±0.2	3.4±0.2

3.2 Optimizing Recipes and Technological Parameters of Curd Snacks

Since the said ingredients have been obtained by dehydration, they contain a certain number of microorganisms in dried state, which keep viable for a long time and can actively develop under favorable conditions [8]. Considering this, we have substantiated and selected the modes of pasteurization of recipe compositions for curd snacks.

The thermal processing (pasteurization and sterilization) is used to keep dairy products from deterioration and prolong their shelf life. At the same time the long high temperature exposure often causes undesirable changes in their components, their physical-chemical, organoleptic, and processing properties. Thus, in all modes of thermal processing the producers try to save all initial properties of dairy products, their nutritional and biological value [9].

The pasteurization of milk protein mixture was performed at 55...60°C during 30 minutes. The temperature interval of pasteurization is determined by the upper protein coagulation temperature limit of 65...67°C, the exceeding of which causes the delamination of the mixture, appearance of clots and graininess.

In this case, the uniformity of the system was unattainable. At a lower temperature the mixing became more difficult because of the increase of the mixture's viscosity due to gelatin forming.

Taking into consideration the defect of consistency caused by heating the mixture up to over 65°C, it is necessary to raise the pasteurization threshold, which does not worsen the final product's quality.

The research has shown that the addition of sodium citrate, which is one of the melting salts and prevents the delamination of the milk protein mixture, allows to perform the pasteurization at 85...90°C. In this case, the duration of the pasteurization can be shortened to (1…3)×60 s.

The choice of the pasteurization mode is determined by the micro-structural changes taking place in the recipe mixture [3], as well as sanitary requirements [8]. The processing temperature lower than 85°C applied for (1…3)×60 s does not provide for the complete bacteriological safety of the final product. The thermal processing at 90°C cause melting of the mass, which is a defect of the final product produced by the developed technology.

We have proposed additional requirements to the primary processing of the raw material aimed at diminishing its microbiological semination. Not more than 10 mm thick layer of apple powder was heated in an oven at (65...70)°C during (15…30)×60 s, (10…15) mm thick layer of salt was heated at (180...200)°C during (30…40)×60 s. The process of structure forming, which follows the pasteurization

and molding, was performed while cooling the mixture down to 6…8°C during 150×60 s.

The results of the microbiological researches have confirmed that for the selected processing modes the microbial number is within the limits acceptable for dairy products. Table 3.3 demonstrates the results of the bacteriological researches of milk protein and culinary products on its base.

Table 3.3 – The results of the bacteriological researches 72 hours after the production of samples

Samples	Product mass, g, in which the following not found			
	E. coli	Salmonella	Proteus	S. aureus
Milk protein	1.0	25.0	1.0	1.0
Salty curd cake	1.0	25.0	1.0	1.0
Sweet curd cake	1.0	25.0	1.0	1.0
Sweet curd cake with sodium citrate	1.0	25.0	1.0	1.0

The data in Table 3.3 confirm the absence of pathogenic microorganisms in the final product samples. This proves the food additions' safety and the possibility of their use in the milk protein based products.

The previous research had allowed to optimize the recipes and determine the rational components percentages, which ensure the final products' best quality indices. Tables 3.1, 3.2, 3.4, 3.5 demonstrate the optimized correlations of content percentages and processing modes.

The analysis of the experimental data makes possible to draw the following conclusions:

-by adding 3% of sugar, 1% of gelatin, 1% of apple powder, 0.5% of sodium nitrate (Table 3.1 column 4, 3.2) we obtained the product with indistinct flavor and weak structure;

-adding 14% of sugar, 3% of gelatin, 9% of apple powder, 1.5% of sodium nitrate (Table 3.1 column 5, 3.2) let us obtain the product with full, elastic consistency of processed (melted) cheese of dark color with excessive flavor of dried apples, no curdling felt;

-the rational organoleptic indices were achieved in curd cakes, whose recipe correlations are presented in columns 2, 3, 4 of Table 3.

Table 3.4 demonstrates the results of the research of producing the milk protein based samples with addition of salt.

Table 3.4 – The correlations of recipe components and processing modes chosen for salty curd cakes production

Raw materials, modes and processes	Amount, %				
	1	2	3	4	5
Milk protein	92.0	88.0	94.0	80.0	6.0
Gelatin	1.0	1.5	2.0	2.5	3.0
Salt	1.0	1.5	2.0	2.5	3.0
Whey	6.0	9.0	12.0	15.0	18.0
Total	100.0	100.0	100.0	100.0	100.0
Mixing duration, s	180	300	360	420	600

Table 3.5 gives the organoleptic evaluation of the quality of salty curd cakes , produced according to various recipes.

Table 3.5 – The experimental evaluation of salty curd cakes

Indices	Recipe variants				
	1	2	3	4	5
1	2	3	4	5	6
Consistency	does not keep shape, spreading, unmixed clots and undissolved sugar crystals	Curdled, keeps shape, no unmixed clots	Elastic, flexible, uniformly even, curdled	Elastic, flexible, curdled	Dense, resilient, elastic, melted, no curdling felt
Color	Light cream	Light cream	Cream	Light brown	Dark, close to brown
Flavor	Sour milk, not salty enough, almost untraceable smack of dried apples	Sour milk, tender, salty with a slight smack of dried apples	Sour milk, tender, salty with a slight smack of dried apples	Sour milk, tender, salty with a slight smack of dried apples	Sour milk, very salty with a distinct smack of dried apples
Aroma	Characteristic of a dairy product	Characteristic of a dairy product	Characteristic of a dairy product	Characteristic of a dairy product	Characteristic of a dairy product
Organoleptic evaluation, points	3.6±0.1	4.8±0.2	5.1±0.2	4.6±0.2	3.3±0.1

The organoleptic evaluation of the experimental cheese cake samples let determine the rational correlation of the components and processing modes, which ensure the best quality.

It is known that the rheological properties of cheese cake masses with various compositions of ingredients depend on protein content and concentration of sugar. The high protein content and absence of sucrose cause the structure to strengthen due to the stronger binding of coagulated particles [10].

The data in Figure 4.1 demonstrate that the 10 % concentration of sucrose, established by us, contributes to weakening the system (sample 3). The penetration degree increases compared to the initial protein increases more than two times, and compared to the milk protein mixed during 7 minutes without adding sugar – 1.2 times.

Thus, the addition of sucrose to the system improves its processing properties and makes mixing the components easier.

The addition of 5 % of apple powder contributes to 1.7 times strengthening of the structure (Figure 3.1, sample 4) of the mixture of milk protein with sucrose.

The results of the organoleptic researches have shown that the addition of less than 1.5 % of gelatin to the milk protein mixture with sugar and apple powder causes the output product to have weak structure. The products with such amount of structure former could not keep shape. Their consistency was spread-like, which prevented portioning.

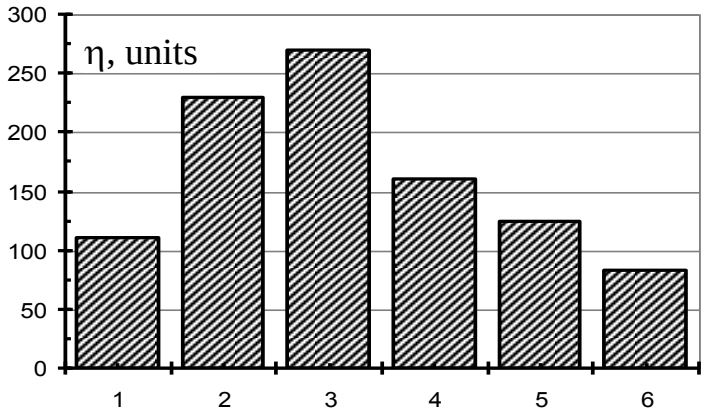

Figure 3.1 – Penetration degree (η) of milk protein masses: not mixed (1) and mixed (2); mixtures of milk protein mass: with sucrose (3), with sucrose and apple powder (4); sweet curd cakes: with gelatin (5), with gelatin and sodium citrate (6)

The addition of gelatin with concentration 1.5% contributed to dense consistency. The organoleptic evaluation of such products showed that the curdling

is not felt in the final product. These products were closer to gel in their consistency than to curd products, which was considered as worsening of quality.

The addition to the system of 2% of gelatin (Figure 3.1, sample 5) causes 1.4 times strengthening of the milk protein mixture. In this case, the output products have similar structural-mechanical properties to the basic milk protein's properties. This proves the rationality of the amount of gelatin in the recipe, established by the results of the organoleptic evaluation.

In accordance with the found acceptable threshold concentrations, the citrate content in culinary products should not exceed 1.0%.

The addition to the recipe mixture with 2% gelatin concentration of 1% of sodium citrate, which we found during the organoleptic evaluation, caused 1.5 times strengthening of the final product's structure (Figure 3.1, sample 6). The organoleptic evaluation has confirmed that such strengthening of the structure lowers the products' quality.

The structural-mechanical research of the milk protein mass with different concentrations have been performed to determine the rational amount of sodium citrate in the recipe mixture. The research has shown that the addition of less than 0.5% of sodium citrate does not greatly influence the structural-mechanical properties of milk protein mass (Figure 3.2).

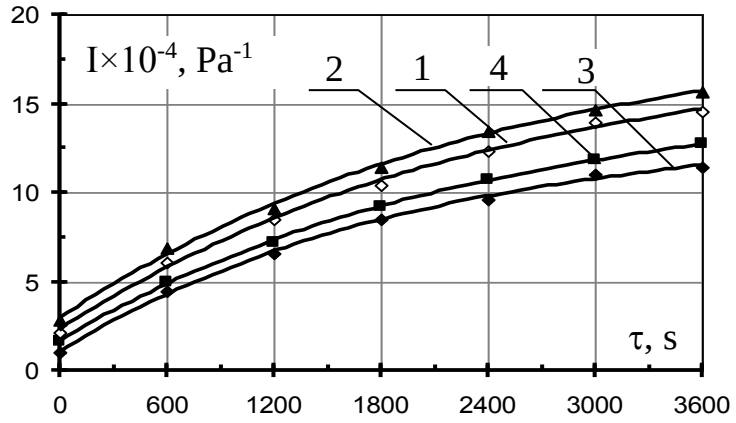

Figure 3.2 – Compliance *I=f(t)* of milk protein mass with sodium citrate concentrations (%): 1, 2, 3, 4 – 0.0; 0.5; 0.75; 1.0 respectively

However, even at this level of its concentration there is no delamination in milk protein mass. The rational organoleptic indices have been obtained when adding 0.75…1.0% of sodium citrate to the system (Figure 3.3).

It has been established (Figure 3.3) that the addition of the relevant amount of sodium citrate allows to diminish the amount of gelatin in the recipe mixture by 15%. In this case, the products' mechanical strength is similar to the control with 2% gelatin concentration without sodium citrate. At this sodium citrate

concentration in the selected processing modes, the products keep their curdled nature.

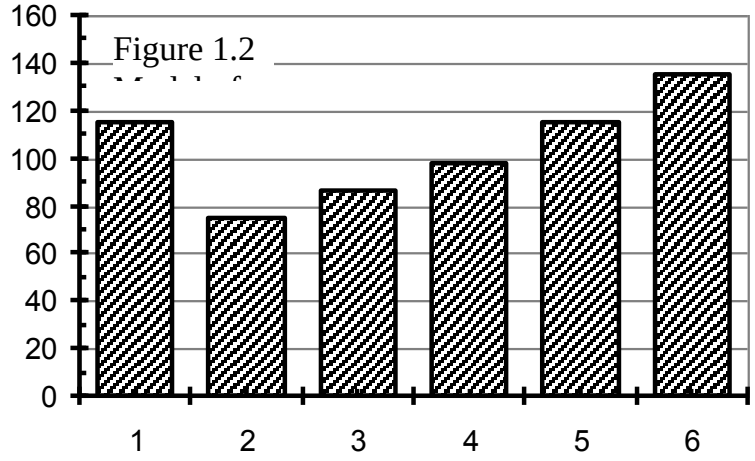

Figure 3.3 – The penetration degree (η) of sweet curd cakes: 1-with 2% concentration of gelatin; 2, 3, 4, 5, 6 - with sodium citrate concentrations 1% concentration of sodium citrate and gelatin (%) - 2; 1.9; 1.8; 1.7; 1.6% respectively

Our structural-mechanical research lets us assume that the system's strength increases on the one hand due to the melting of the protein mass and agglomeration of protein molecules [3], and on the other hand due to a change in gelatin's functional properties [1, 2].

The further research was directed towards the use of moisture-binding additions in culinary recipes with milk protein.

It is known that bound water, as opposed to free water, is inaccessible to microorganisms. Thus, the additions to our researched system designed to give the system certain functional and technological properties impede the development of microflora, because they bind water well [9].

Taking into consideration that the basic product has 66% of moisture, and the selected additions somehow differently contribute to transforming moisture to bound state, their value is obvious.

The thermograms of the milk protein samples with different compositions were taken to determine the influence of 0.75…1.0% of sodium citrate in the selected pasteurization mode on the state of water in the mixture.

The thermal process of heating is accompanied by a whole range of physical and chemical processes. If there is water in the system, then first it evaporates with consuming heat [11]. The state of water in the system may be quantitatively characterized by the temperature of evaporation, which is calculated according to the thermographic curves [12, 13].

In general, the heat of vaporization of any substance can be the measure of strength with molecules of this substance among themselves and with the molecules of other substances [12].

In the area of low pressures of vapor (when it may be regarded as ideal gas) the heat of vaporization changes rather slightly with the temperature, however, it lowers with the temperature increase.

It is known that the heat of vaporization of water depends on temperature to a certain extent, though in many researches with not very large temperature intervals it is assumed as constant [12, 13].

Figure 3.4 shows the correlations *ln li = f(-1/T*), which according to equation 2 have a distinct linear character. Correlations 1..3 in this figure correspond to the thermograms.

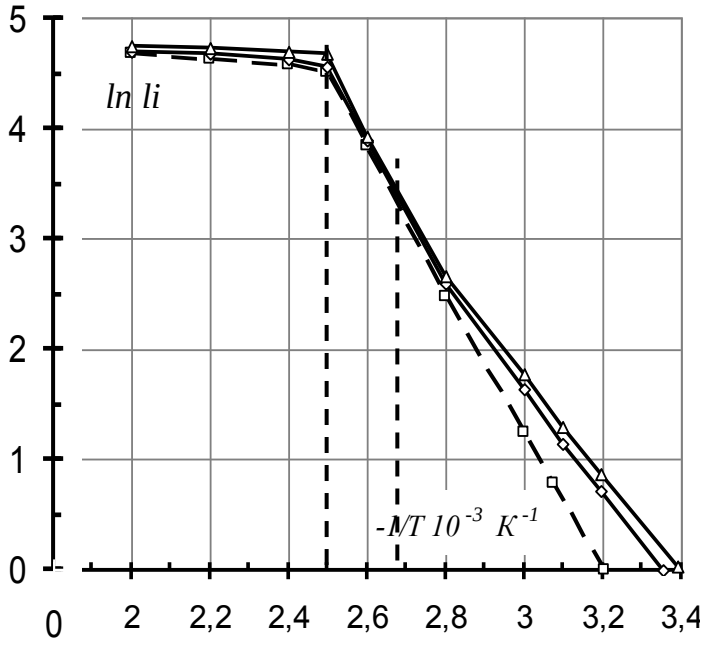

Figure 3.4 The dependence of *ln* value, proportional to moisture loss of milk protein mixtures *ln li = f(-1/T*) on the temperature: 1 – for sweet curd cakes; 2 – for sweet curd cakes with sodium citrate; 3 - for salty curd cakes

The analysis of the dependence *ln li = f(-1/T*) shows that for all researched compositions of protein mixture one can determine 3 temperature intervals with sharp discrepancies between the heat of vaporization and binding energy of water. The sharp change of the heat of water vaporization at certain temperatures points at the qualitative change of the state of water in the system [14].

These correlations help observe clearly the effect of the milk protein mixture’s composition on the binding energy of water with other components of the system.

The calculation of the heat of water vaporization according to the thermograms of pure water has shown that sharp changes of the heat of vaporization from the surface , which are observed in researched samples, cannot be due to dependence of Q_{vap} on T. The changes of Q_{vap} due to temperature in the samples are caused by the change of energy of binding water by the substances of the system.

The research has established a certain correlation between the energy of binding water and the penetration degree (Table 3.6).

Table 3.6 – The heat of vaporization and binding energy of water in curd cakes with different compositions of milk protein mixtures

Purpose and composition of mixture	Heat of vaporization Q_{vap}, кJ/mole			Binding energy of water, E_{bind}, кJ/mole		
	Temperature interval, K					
	298... 373	373... 398	398... 498	298... 373	373... 398	398... 498
Mixture for sweet curd cakes (milk protein - 72%, sugar - 10%, apple powder - 5%, gelatin - 2%, whey -12%)	34.8	68.5	7.3	31.7	65.2	3.2
Mixture for sweet curd cakes (milk protein - 72%, sugar - 10%, apple powder - 5%, gelatin - 2%, whey -12%, sodium citrate - 1%)	51.2	51.2	12.2	48.1	47.9	8.1
Mixture for salty curd cakes (milk protein - 87%, salt - 2%, gelatin - 2%, whey - 12%)	39.3	72.4	8.2	36.2	68.3	4.1

As Table 3.6 shows the binding energy of water in the system with sodium citrate in the area of heating up to 373 K considerably increases compared to mixtures without sodium citrate. It lets us assume that the change of the state of water in the system is obviously caused by its redistribution among the components of the milk protein colloidal system.

Thus, the addition to the system of 0.75…1.0% of sodium citrate in the selected processing modes contributes to transforming moisture into bound state in

a greater extent than by adding sugar and apple powder for sweet curd cheese cakes production and salt for salty curd cakes production.

The increase of the binding energy of water in the milk protein mixture with sodium citrate may be explained by the effect of this salt on the conformational state of milk protein and gelatin molecules. It has been established [1,2] that gelatin can interact with anions of citric acid on the level of molecular forces, and have such changes of the state of its molecules that cause hydrophilic areas to free from intermolecular interactions. If it may be assumed that sodium citrate affects milk protein in this way, then it may be possible to explain the increase in its swelling and moisture absorption in the presence of this salt. Thus, sodium citrate raises milk protein's moisture-retaining capability.

As a rule, the binding energy is much higher at low temperatures, than at high temperatures [12]. However, in the samples lacking sodium citrate the binding energy grows considerably when the temperature reaches boiling of free water. When the temperature keeps on rising, it moves practically to zero in all cases. It may be explained by gelatin's capability to form a film preventing moisture vaporization.

The linear area of dependence *ln li-f (-1/T)* throughout the whole heating area up to the area where the heat of water vaporization and its binding energy decrease allows to state that film does not form in the presence of gelatin in the system with gelatin. This probably will have a positive effect on the quality of products in selected temperature modes of pasteurization, because the rise of the temperature up to 90°C in the reverse case can lead to the formation of dehydrated crust, which will make processing more complicated.

The organoleptic indices of quality of curd cakes with sodium citrate are as high as those of products without sodium citrate, and its capability to raise milk protein's moisture-retaining properties can contribute to increasing microbiological stability, which also confirms the rationality of its addition to the system with dry additions.

3.3 Working out the Process Flowchart of Curd Cakes Production

The performed experiments have led us to developing the technology of culinary products on the base of milk proteins obtained by the thermoacid coagulation method.

The raw materials (sugar, salt, apple powder) were freed from mechanical impurities by sifting. Not more than 15 mm thick layer of apple powder was heated at (65…70)°C during (15…30)×60 s, (10…15)mm thick layer of salt was roasted

at (180...200)°C during (30…40)×60 s. Whey was strained. Gelatin was washed in cold water 2…3 times, then whey was poured at (+18...+20)°C in proportion of 1:6, and it was left to soak and swell during (40…60)×60 s.

Sodium citrate was added to the calculated amount of water to obtain 58% solution, and the solution was brought to boiling.

According to recipes the components were mixed with the obtained milk protein and stirred to uniform consistency during 20…30 min. Then gelatin dissolved at (55…65)°C was added, and the mixture was heated at (55…65)°C while constantly stirred during (30…60)×60 s.

When producing sweet fruit curd cakes with sodium citrate the mixture was heated up to (85…90)°C and kept at this temperature while constantly stirred during 1..3 min.

The curd cake mass was put on a flat surface in a layer of 35±2 mm and cooled at (6…8)°C till forming flexible elastic consistency during 150×60 s.

Figures 3.5, 3.6 show the process flowchart of sweet curd cakes production; Figure 3.7 - salty curd cakes production.

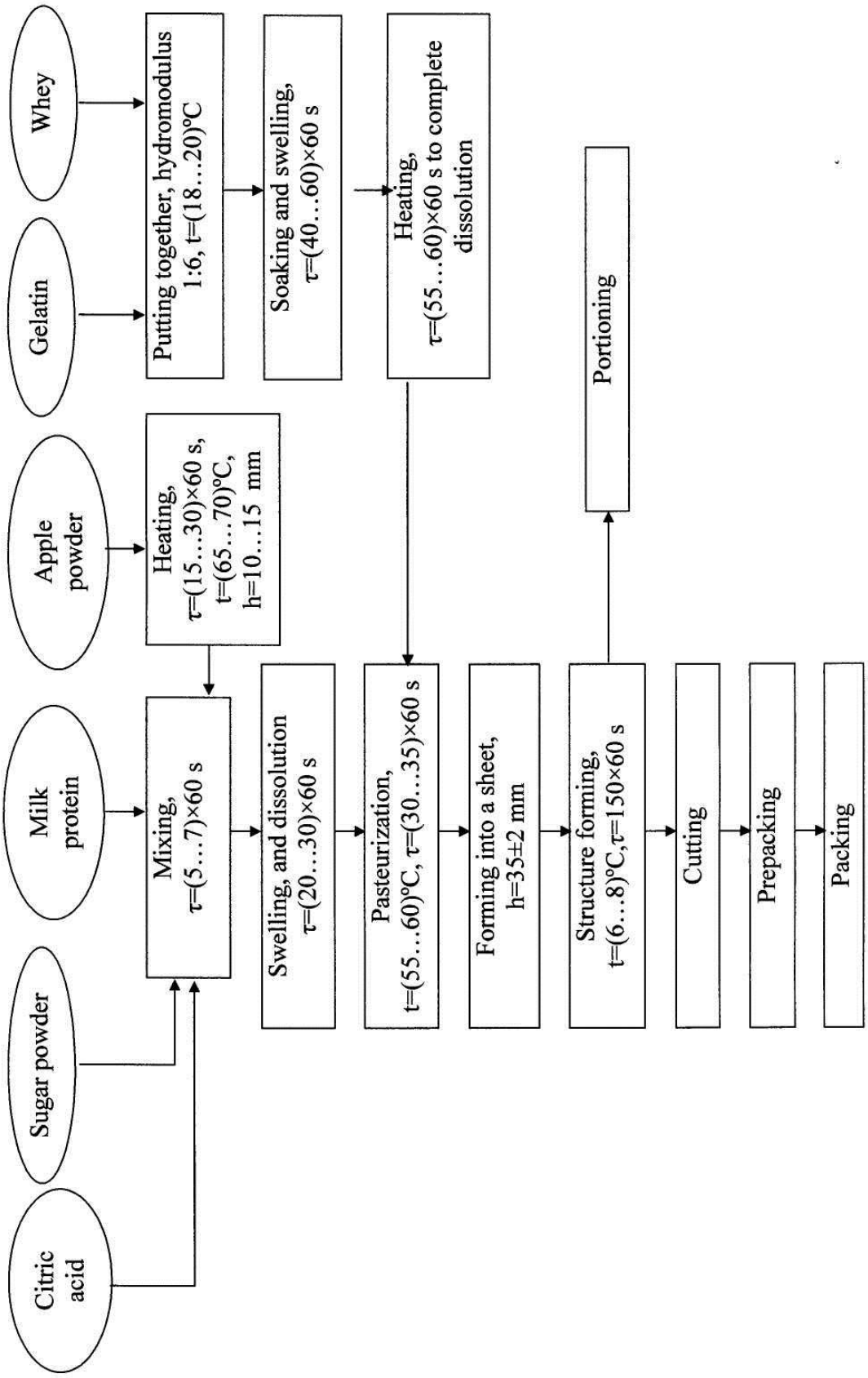

Figure 3.5 – The Process Flowchart of Sweet Fruit Curd Cakes Production

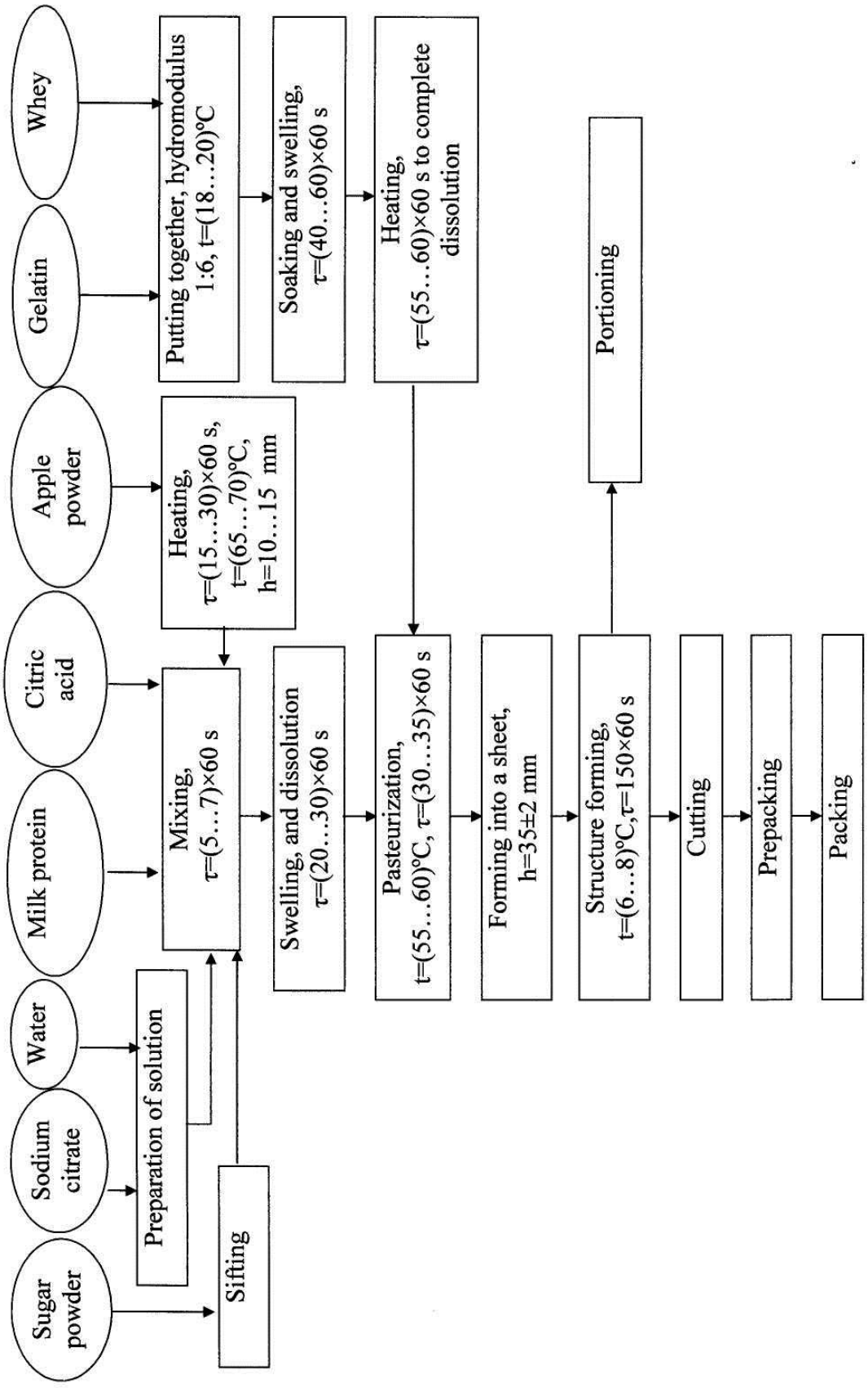

Figure 3.6 – The Process Flowchart of Sweet Fruit Curd Cakes Production with Sodium Citrate

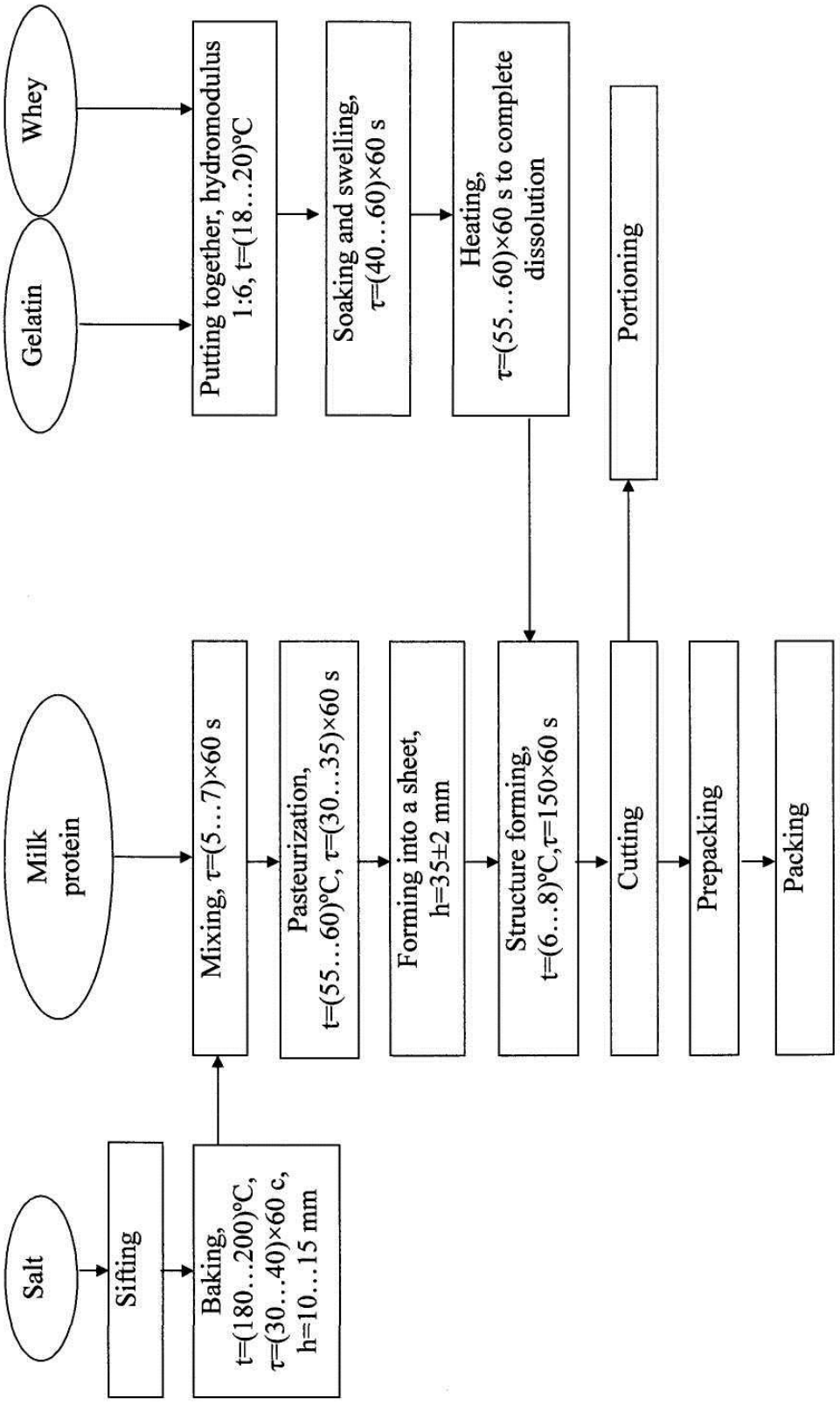

Figure 3.7 – The Process Flowchart of Salty Curd Cakes Production

3.4 Investigation of the Quality Attributes of Culinary Products on the Base of Milk Protein

The previous research allowed to select the rational variant of recipe composition and process technology of production of curd cakes on the base of milk protein. We have proposed two recipe variants. The first one does not use sodium citrate, and pasteurization was performed at (55...65)°C during (30...35)×60 s. In the second one sodium citrate was used, and pasteurization was performed at (85...90)°C during (1...3)×60 s. The purpose of the research was to establish the effect of temperature, duration of pasteurization, and additions on the nutritional value of finished products.

Table 3.7 shows the research data on the chemical composition.

Table 3.7 – The chemical composition of curd cakes

Indices	Finished products		
	Sweet fruit curd cakes	Sweet curd cakes with sodium citrate	Curd mass
Solid, g/%	41.1±1.1	41.2±0.9	45.3
Proteins: g/% in solid	 13.9±0.6 33.9±1.5	 12.5±0.8 30.4±1.9	 12.1 26.7
Fats: rg% in solid	 11.0±0.7 25.8±1.7	 11.6±0.5 28.2±1.2	 15.6 34.4
Carbohydrates: g/% in solid	 14.8±0.4 35.0±1.0	 15.0±0.6 36.4±1.5	 15.9 35.1

The investigation of the chemical composition has shown that in sweet curd cakes the protein content in solid is 3.7…7.9% higher than in curd mass with sugar, despite the fact that curd content in curd mass is 90% [14]. It is higher by 27%, than in curd cakes.

When 10% of sugar was added, it was found that the sugar content in the curd cakes' recipe was 14%. Thus, the amount of added sugar decreased by 40% due to the sugars retained in apple powder. In this case the total hydrogen content in sweet curd cakes' solid is 0.9…1.3% higher than in curd mass with sugar, though the amount of sugar in their recipe is 4% lesser.

The nutritional value of any product is higher the more it satisfies organism's demand in nutritional substances [15, 16, 17].

Table 3.8 shows the percentage of satisfying the daily need in nutritional substances by curd cakes.

The data in Table 3.8 show that 100 g of curd cakes satisfy 24…28% of daily need in proteins of animal origin. This allows assuming the high protein content in curd cakes. In this case (14…17)% is satisfied by essential amino acids. Comparing the percentage of their satisfying the daily need in protein to other products, it can be noted that it is rather high. In their protein content curd cakes are not inferior to such products as meat (18…20)%, eggs (12…13)%, cheese (14…18)% [14, 18, 19].

Table 3.8 – Percentage of satisfying the daily need in nutritional substances by 100 g of curd cakes

Nutritional substances	Daily need, g.	Content in 100g of curd cake, g	Need satisfaction, %
Proteins,	80…100	12…14	12…18
including animal proteins	50	12…14	24…28
essential amino acids	29…36	5	14…17
Fats,	80…100	11…12	11…15
including animal fats	48…60	11…12	18…25
essential polyunsaturated fatty acids	2…6	0.66…0.96	11…48
Carbohydrates,	400…500	15	3…4
including mono- and disaccharides	50…100	15	15…30
ballast substances (cellulose and pectin)	25	0.35	1.4

We should also note a high percentage of satisfying the daily need in animal fats 18…25%, taking into consideration the high biological value of milk fat. In this instance 11…43% are covered by polyunsaturated fatty acids.

The percentage of satisfying the daily need in carbohydrates is low, but nevertheless, higher than in milk protein without additions. We may note the presence of ballast substances, by which dairy products have been enriched recently [20]. Moreover, the percentage of satisfying by mono- and disaccharides is 15…30%.

The nutritional value of a product is determined by calculating the conformity percentage for each of the most essential components according to the balanced diet equation.

Table 3.7 shows that the protein, fats, and carbohydrates ratio in sweet curd cakes is 1:0.8...0.9:1.0...1.2 respectively, while in milk protein it is 1:0.9:0.06. Similarly, in curd cakes the ratio of fat and protein is close to rational 1:1:4 or 1:0.8:3.5…4 [15, 19]. The amount of carbohydrates increases due to the addition of sugar and apple powder to the milk protein mass. The carbohydrate imbalance is taken into consideration in the development of culinary products with the use of curd cakes. Fresh, stewed, and tinned fruit and vegetables are used as garnishes and side dishes, which helps increase the carbohydrate content. The use of starchy raw materials, such as bread for open sandwiches or potatoes for salads, helps increase the starch content in recipes. In addition, the use of vegetables and fruit helps enrich dishes with dietary fiber and pectin substances, as well as vegetable proteins, despite that fruit and vegetables contain small amounts of protein. The use of vegetable oils, mayonnaise, salad dressings in recipes helps enrich culinary products with vegetable fats. The use of green peas and nuts in recipes raises vegetable protein content.

The performed research has shown that the thermal processing with the purpose of pasteurization does not considerably affect the protein content. The calculations show that there is almost no protein loss (Table 3.9).

Table 3.9 – Fractional composition of protein in curd cakes

Product	Casein			Whey proteins		
	% of total protein	% in 100 g of product	% of solid	% of total protein	% in 100 g of product	% of solid
Sweet curd cakes	85.0±3.6	11.8±0.5	28.8±1.2	14.0±0.7	2.0±0.1	4.8±0.2
Sweet curd cakes with sodium citrate	85.0±4.8	10.6±0.6	25.8±1.5	14.0±1.6	1.8±0.2	4.3±0.5
Sweet curd cakes	77.4±2.5	12.2+0.4	33.4±1.1	11.6±0.6	1.8±0.1	5.0±0.3

As Table 3.9 shows, the addition of sodium citrate and raising the pasteurization temperature do not cause any notable decrease of casein and whey proteins. An insignificant decrease of proteins in this case may be due to forming

and aggregating flavoring and light aromatic substances. The addition of sodium citrate contributes to this [21].

Table 3.9 shows that in general curd cakes are characterized (in percentage of total protein) by high content of casein (75…85) % and whey (12.0%, 14.0%), which cannot be said of products from curd cake masses lacking whey proteins.

The modern theory of balanced nutrition allows to estimate food products not so much quantitatively, as qualitatively. Protein quality is estimated taking into consideration its amino acid composition and content [22].

The main reason of reduced availability of amino acids is their excessive heat processing. Great damage is done at higher temperatures, especially during long exposure [18], which is the case of manufacturing products on the base of milk protein in different modes of thermal treatment.

The comparison of milk protein-based products' amino acid composition in different temperature modes and at various durations of pasteurization has been done to determine the effect of pasteurization on their nutritional properties (Table 3.10).

Table 3.10 – Amino acid composition of protein in curd cakes

Amino acids	Sweet fruit curd cakes		Sweet fruit curd cakes with sodium citrate	
	g/100g	% in solid	g/100g	% in solid
1	2	3	4	5
Essential amino acids				
Total:	4.949	35.4	4.856	38.82
Valine	0.792	5.61	0.764	6.25
Isoleucine	0.698	5.02	0.734	5.92
Leucine	1.047	7.38	0.952	7.57
Lysine	0.713	5.02	0.650	5.26
Methionine	0.363	2.66	0.352	2.96
Threonine	0.622	4.43	0.660	3.29
Phenylalanine	0.714	5.02	0.744	5.92
Replaceable amino acids				
Total:	8.361	59.89	7.450	59.55
Alanine	0.623	4.43	0.952	4.61
Arginine	0.488	3.54	0.489	3.95
Asparaginic acid	1.095	7.97	0.952	7.57
Histidine	0.362	2.66	0.389	2.96

1	2	3	4	5
Glycine	0.630	4.43	0.552	4.28
Glutaminic acid	2.448	17.70	2.137	17.11
Proline	1.213	8.85	1.024	8.23
Serine	0.812	5.9	0.766	6.25
Tyrosine	0.658	4.72	0.509	3.95
Cystine	0.032	0.25	0.040	0.32

The performed research has demonstrated that the thermal processing does not effect the amino acid composition. The essential amino acids content is 37…40%, which is characteristic of fully valuable proteins [14, 19].

The investigation of the amino acid score of curd cakes' proteins (Table 3.11) has shown that the amino acid score of the essential amino acids is rather high. It is worth mentioning that the milk protein content in sweet curd cakes recipes is 7.2%, and the additions used contain insignificant amount of amino acids.

Table 3.11 – The amino acid score of proteins in curd cakes

Essential amino acids	Levels recommended by FAO/WHO		Sweet curd cakes with gelatin		Sweet curd with sodium citrate	
	mg in 1g ideal protein	% of scale	mg	%	mg	%
Lysine	55	100	51.3	93.2	52.0	94.5
Valine	50	100	57.0	11.0	61.1	122.2
Isoleucine	40	100	50.2	125.5	58.8	146.8
Leucine	70	100	75.3	107.6	76.2	108.8
Phenylalanine + Tyrosine	60	100	98.7	164.5	100.2	167.1
Threonine	40	100	44.7	111.9	52.8	132.0
Methionine + Cystine	30	100	28.4	81.2	31.4	89.6

The reduction of the percentage of amino acids, which are present in protein in excessive amounts, reduces the imbalance, because on the background of the heightened content of certain amino acids there is the increase of imbalance of limited amino acids – lysine, methionine, and cystine.

It is not enough to estimate the nutritional value of Table 3.12 by the biological value of proteins. It is necessary to know if there are lipids and what

their fatty acid composition is, and if there are carbohydrates, vitamins, micro- and microelements.

Table 3.12 shows the experimental data on lipid content.

Table 3.12 – The fatty acid content of lipids in curd cakes

Fatty acids	Curd cakes with gelatin	Curd cakes with sodium citrate
1	2	3
Saturated	58.25	54.77
$C_{8:0}$ (caprilyc)	2.61	2.68
$C_{10:0}$ (capric)	1.42	1.14
$C_{12:0}$ (lauric)	3.50	2.70
$C_{14:0}$ (myristinic)	8.68	8.23
$C_{14:0}$ (isomyristinic)	0.67	0.75
$C_{15:0}$ (pentadecanoic) $C_{16:0}$ (palmitic)	24.78	25.35
$C_{16:0}$ (isopalmitic)	0.94	0.77
$C_{17:0}$ (margarine)	1.40	1.22
$C_{18:0}$ (stearic)	12.3	10.05
Unsaturated, including: monosaturated	41.75	45.23
$C_{10:1}$ (caproleic)	1.26	1.03
$C_{12:1}$ (lauric)	1.06	0.91
$C_{14:1}$ (myristinic)	1.65	1.63
$C_{16:1}$ (palmitoleic)	3.22	3.18
$C_{17:1}$	1.11	1.45
$C_{18:1}$ (oleic)	27.43	28.72
polyunsaturated:		
$C_{18:2}$ (linoleic)	3.67	5.32
$C_{18:3}$ (linoleni.)	2.35	2.99

The analysis of the data in Table 3.12 has shown that in the composition of curd cakes' lipids there are 18 fatty amino acids with the number of atoms of carbon from C_8 to C_{18}. The ratio of saturated and unsaturated acids remains practically the same as in milk protein fat. There are more saturated fatty acids, whose content is 55…58%. The composition of fatty saturated acids is characterized by 25%, 9%, and 10...12% of palmitic, myristinic, and stearic ones respectively in proportion to the total content of fatty acids.

The unsaturated fatty acids make up 42…45%. Most of it is oleic acid, which stands for 29% of the total content of fatty acids.

The percentage of polyunsaturated fatty acids is 6…8%.

The analysis of the fatty acid composition of the milk protein mass and curd cakes has shown that there is a slight redistribution of certain fatty acids in their triglycerides composition. In general, their content is characteristic of milk fat. It is determined by the fact that besides milk protein in the recipes of curd cakes there are no other fat-containing components.

The use of milk fat for curd cakes production allows to increase the content of fatty acids without adding butter.

However, it is worth mentioning that the final product does not have enough polyunsaturated fatty acids. But despite the low level of polyunsaturated fatty acids, curd cakes, which contain vitamins A, D, E, are products of high nutritional value [23].

The analysis of the fatty acid content of milk protein and curd cakes has shown the lipid composition does not considerably change in the process of curd cakes production. The presence of sodium citrate in their recipes and the pasteurization modes do not affect the fatty acid composition of final products, too.

The raw materials containing vegetable fats may be added to the composition of culinary products with curd cakes. It will increase the amount of polyunsaturated fatty acids.

It is known that the sufficient fat intake by organism affects the digestion of vitamins and provitamins (E, K, beta-carotene), which arrive with vegetable food [24]. It is an advantageous characteristic of the obtained product over defatted ones.

Taking into consideration the milk fat's properties and its high digestibility curd cakes may be used as ingredients of culinary products for dietary and child nutrition.

The semiquantitative spectral analysis of curd cakes has shown that their sol part contains a great number of macro- and microelements (Table 3.13).

Table 3.13 – The mineral composition of sweet fruit curd cakes (% of solid)

Mineral elements	Curd cakes with gelatin	Curd cakes with sodium citrate
1	2	3
Calcium	20.0	20.0
Magnesium	3.0	3.0
Sodium	0.6	0.6
Phosphorus	-20.0	-20.0
Strontium	<0.01	<0.01

1	2	3
Iron	0.003	0.003
Manganese	<0.0005	<0.0005
Silicon	0.003	0.003
Aluminum	0.004	0.004
Titanum	0.002	0.002
Copper	0.0003	0.0003
Cobalt	<0.0001	<0.0001
Nickel	<0.0001	<0.0001
Chromium	<0.001	<0.001
Lead	<0.0005	<0.0005
Tin	<0.0005	<0.0005
Antimony	<0.01	<0.01
Barium	<0.001	<0.001
Boron	<0. 03	<0.03
Beryllium	<0.0001	<0.0001
Arsenic	<0. 03	<0.03
Molybdenum	<0.0005	<0.0005
Zinc	<0. 005	<0.005
Iodine	<0.0008	<0.0008
Ytterbium	<0.0003	<0.0003
Cerium	<0.01	<0.01
Cadmium	<0.001	<0.001
Zirconium	<0.0003	<0.0003
Scandium	<0.0005	<0.0005
Vanadium	<0.0003	<0.0003
Bismuth	<0.0003	<0.0003
Galium	<0.0001	<0.0001
Indium	<0.0005	<0.0005
Germanium	<0.00005	<0.00005
Silver	<0.00005	<0.00005
Mercury	<0.01	<0.01

Ca, Mg and P are the leading elements in sol part of the obtained products. Iron, copper, manganese, cobalt, and iodine must be mentioned among their microelements.

The analysis of the data in table 3.13 has shown that in the limiting accuracy of the method the amount of calcium, magnesium, sodium, iron, aluminum increased, obviously, due to their presence in apple powder [4] and gelatin [18].

The use of curd cakes for making culinary products will make it possible to enrich the diet with presently deficient mineral substances, such as calcium and iron [24].

The obtained data on mineral composition of new products allow to modify the composition of dietary intake according to changing demands of organism in mineral substances depending on physiological reasons due to good compatibility of curd cakes with a diverse assortment of products, sources of various mineral elements.

The data in Table 3.13 demonstrate that the pasteurization modes do not diminish the mineral substances content in the product.

Despite the positive effect of mineral substances on different processes taking place in organism, there are norms of their contents in products, because their excess may have toxic effect. The table demonstrates that when the proposed additions are used in the curd cakes' recipes, the heavy metal content is within the acceptable limits for food products and do not limit the use of curd cakes in nutrition.

The investigations of vitamin composition have shown that curd cakes contain a substantial amount of fat-soluble vitamins (Table 3.14).

Table 3.14 – The content of fat-soluble vitamins in sweet fruit curd cakes

Name of product	Content of fat-soluble vitamins, mcmole/g				
	A	D	E	F	K
Curd cakes with gelatin	0.034±0.09	0.41±0.02	0.56±0.02	2.90±0.41	0.50±0.06

The calculations let us establish that the pasteurization at 55…60°C during 30 minutes causes the reduction of the vitamin content: the loss of vitamin A was 1…5%, vitamin E – 9.0% with the increase of the content of oxidated and semi-oxidated forms.

The carotene content in the products did not reduce. Probably, the fat-soluble vitamins content diminished due to their oxidation in the process of mixing during pasteurization, because the vitamins of this group easily oxidize in contact with oxygen.

Table 3.15 shows the content of water-soluble vitamins in sweet fruit curd cakes.

The data of Table 3.15 demonstrate that curd cakes are a good source of vitamin B_2, whose content is 0.65…0.80 mg%, and have a poor content of PP

(1.0…2.0%). The use of apple powder let increase the water-soluble vitamins content.

Table 3.15 – The content of water-soluble vitamins in sweet fruit curd cakes

Name of product	Content of water-soluble vitamins, mcmole/g		
	B_1	B_2	PP
Sweet curd cakes with gelatin	0.10±0.01	0.65±0.02	1.94±0.05
Sweet curd with sodium citrate	0.15±0.01	0.81±0.03	1.00±0.06

The main objective set during thermal processing was the maximal preservation of vitamins. The research and calculations have established that mild thermal processing lets preserve their considerable content in the product.

It is also worth mentioning that lactic acid is one of the stabilizers, which renew the oxidized form of vitamins. It is probable that the reduction of dehydration of milk protein mass at reduced coagulation temperatures, and the use of whey in curd cakes production contributes to preserving vitamins due to the presence of lactic acid in whey. Pectin substances and sugar are stabilizers [9, 21], which once again confirms the rationality of choosing the proposed additions.

3.5 Organoleptic evaluation scale

The organoleptic evaluation scale has been worked out to control the quality of the developed products at the production and commercialization stage (Table 3.16).

Defects, which deteriorate the quality of the final product, may appear during production. Possible defects and their causes are the following:

- consistency is weak, spreading, grainy, with delamination, whey release, and compressed dense areas. The cause is failure to comply with the recipe composition and exceeding the recommended temperature of pasteurization;
- cracks and drying crust on the surface of the products may be caused by failing to adhere to storage conditions;
- indistinct or foreign flavor and aroma. The cause is failure to comply with the recipe, the use of poor quality raw materials, violation of of conditions and terms of storage.

Table 3.16 The scale of the organoleptic evaluation of sweet fruit curd cakes

Indices	Characteristics of products, points			
	5	4	3	2
Appearance	Even surface, evenly colored	Even surface, evenly colored, acceptable small grains	Acceptable small cracks. Slightly deformed product, unevenly colored surface with grains and unkneaded traces	Deformed products with large cracks and unkneaded traces
Consistency	Elastic flexible, uniform, curdled	Elastic flexible, noy dense, curdled with small grains	Loosely spreading, uneven, delaminates, with large grains and compressed areas	Loose, products don't keep shape, with large grains and compressed areas
Color	Cream	Indistinct light cream, acceptable small grains	Off-cream, uneven with unkneaded traces	Uncharacteristic color
Aroma	Characteristic of dairy product, without foreign aromas	Characteristic of dairy product, light vanilla aroma	Indistinct	Unpleasant, sour, not characteristic of dairy product
Flavor	Sour milk, sweet, with smack of dried apples	Indistinct flavor of dried apples	Weak, indistinct flavor of dried apples	Smack of poor quality raw material

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Chapter 4. Scientific Substantiation of the Technology of Snack Pastes on the Base of Lactic Acid Curd

4.1. Substantiation of the model systems' component selection

4.1.1. Selection and substantiation of the concentration of lactic acid curd as protein base

New food products produced on the base of milk protein are winning a growing segment of the food market and a more importantant place in people's diet.

The analysis of the market of snack pastes has shown a poor assortment of pastes on the base of hard and soft cheeses, the use of milk fat or milk fat combined with vegetable oil, and partial use (up to 20%) of lactic acid curd in recipes [1…14].

It is worth mentioning that the market practically lacks the pastes on the base of fat-free lactic acid curd with additions of vegetable oil as the main fat component. In our view, the main problem of marketing this product manufactured industrially is the lack of scientific foundations of its processing.

The application of scientific principles of substantiation of the use of fat-free lactic acid curd, which is a source of functional protein, on the one hand, will raise the efficiency of the technology due to decrease of expenditure for preparing the protein base, and on the other hand, will ensure its social importance as to raising the final product's quality due to calorie and nutritional value control.

Within the scope of the developed working hypothesis and strategy for the use of vegetable refined deodorized oil in this technology it is important to substantiate the processing conditions and parameters, which will ensure activation of proteins, their transformation into solute state, augmentation in disperse environment of hydration and concentration of proteins, which will play the role of surfactant substances at the stage of emulsification to make easier the dispersion of the fatty phase and obtaining stable emulsion.

The stability of protein-fat emulsion during thermal processing and storage can be provided for by increasing the energy potential of the protein base under effect of alkaline regulators of pH, transforming proteins into a more hydrated state, and providing for their solubility during freeing calcium, which can participate in forming spatial grid, from casein calcium phosphate complex (CCPC), as well as by adding sulfited polysaccharides for binding free moisture and stabilizing the product's structure on the whole.

Taking into consideration the equilibrium state of the colloidal "protein-water" system, which is CCPC, and protein's liability to denature during heating,

the performed research has established (Figure 4.1) that the increase of protein base's hydrophilic capability to 75% provides for the aggregative balance and stability of protein during heating within 70…95°C.

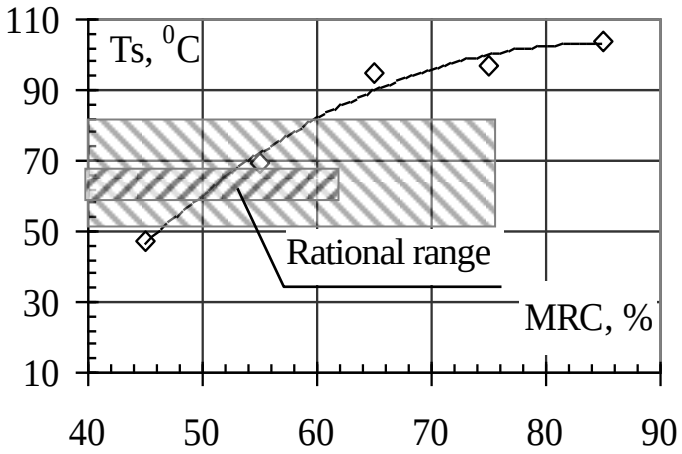


Figure 4.1. The dependence of the protein base's stability on MRC

Moisture-retaining capability (MRC) was taken as the criterion to estimate the increase of the hydrophilic capability of the snack paste's protein base (Figure 4.1). To determine the dependence of lactic acid curd's moisture-retaining capability on pH we researched the changes of the protein base's buffer capacity due to changes in protein's energy state.

To substantiate the ion exchange mechanism we researched the protein hydration changing the protein base's active acidity towards neutrality with the help of substances capable of precipitating polyvalent ions: sodium bicarbonate, trisodiumpolyphosphate, and calcium hydroxide (Figure 4.2).

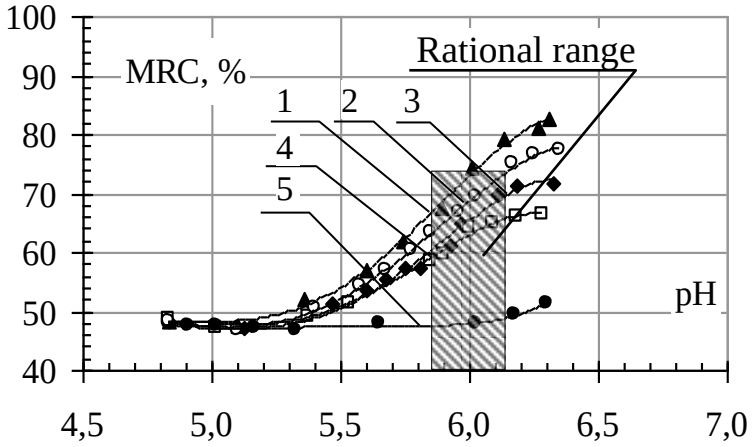


Figure 4.2. The dependence of the protein base's MRC on active acidity 1 – Na bicarbonate, 2 – trisodiumpolyphosphate, 3 – Na hydroxide+Na citrate, 4 – Na citrate, 5 – $Ca(OH)_2$

It has been established that the addition to the system of sodium bicarbonate in the interval of active acidity pH 4.8…6.2% does not cause breaking "calcium

bridges". In this case, the protein base's buffer capacity does not grow and remains 48±1%. There is an increase of active acidity and MRC, when reagents, which contain Na^+ cations, are added to the snack paste's protein base [4, 15, 16, 17].

The analysis of the performed researches (Figure 4.2) has shown that when sodium bicarbonate, trisodiumpolyphosphate, and sodium citrate are added the active acidity of the snack paste's protein base rises within pH 5.0…6.2. At first the MRC is growing slowly from 48±1% to 54±2% within the interval of pH 5.0…5.5, and then considerably increases from 54±2% to 78±2% within the interval of pH 5.5…6.2.

The curves of the protein base's MRC dependence on pH confirm the role of Na^+ cations in breaking "calcium bridges" and increasing MRC from48±1% to 78±2% within the interval of pH 5.0…6.2. Active acidity is of special importance after pH 5.5, which marks the beginning of a considerable increase of MRC.

Thus, the enhancement of the protein base's negative charge was attained by shifting the isoelectric point towards neutrality from 4.8±0.2 to 6.0±0.2, which contributed to increasing its buffer capacity to 80±2% (Figure 4.2) and thermal stability to 95±2^{0}C (Figure 4.1), which conforms to the main principles of the working hypothesis of developing the technology of the snack pastes on the base of fat-free lactic acid curd [4, 5].

To determine the rational concentration of the protein component for its further use in the process of emulsification we have performed the research of the viscosity of the protein base with different contents of fat-free lactic acid curd (Figure 4.3).

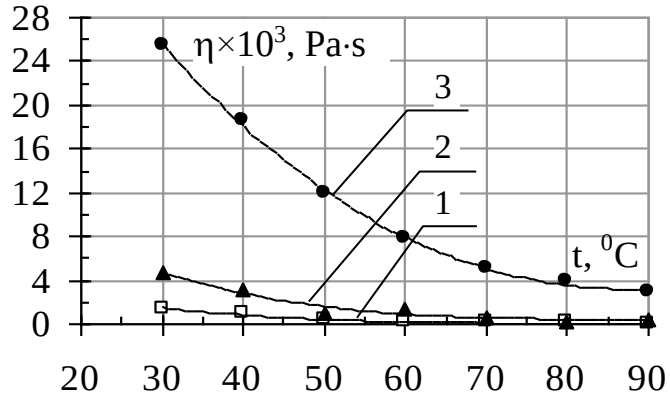


Figure 4.3. The dependence of the viscosity of the snack paste's protein base on temperature with the content of fat-free lactic acid curd: 1 – 30%; 2 – 40%; 3 – 50%

It has been established that when the concentration of fat-free lactic acid curd is 30, 40%, within the temperature range of 90…60^{0}C the viscosity does not

considerably differ and is ~$80 \cdot 10^{-3}$ Pa·s. Lowering the temperature within the 50…30^0C interval causes the increase of the system's viscosity within 100…$420 \cdot 10^{-3}$ Pa·s. Increasing the content of fat-free lactic acid curd in the protein base to 50% causes a notable increase of viscosity in the temperature range of 90…60^0C within 300…$800 \cdot 10^{-3}$ Pa·s, and a considerable increase within 1200…$2580 \cdot 10^{-3}$ Pa·s in the temperature range of 50…30^0C.

Thus, we believe that to use fat-free lactic acid curd in the technology of the snack paste it is necessary to activate the protein with the objective of increasing its water-binding activity. The protein is to hydrate additionally if the number of hydrophilic groups increases as result of the relevant reaction or if these groups come into a contact with water when a change of the protein molecules' conformation takes place. Such conditions appear when pH of the environment grows (correction of active acidity) due to adding different reagents (sodium bicarbonate, sodium citrate, etc.), whose Na^+ ions partially exchange with protein base's Ca^{2+} ions. Taking into consideration that the active acidity of freshly-made lactic acid curd is within pH 4,8±0,2 [18, 19, 20], sodium bicarbonate, which can ensure the necessary ion exchange due to hydrolysis (Figure 4.2) and augment protein's buffer capacity, may be used as an active acidity corrector for the protein base.

4.1.2. Selection and Substantiation of the Concentration of pH Active Acidity Corrector and Melting Salt

When melting salt is selected, it is necessary to take into consideration its activity and the protein raw material's properties. There are several fractions of nitrogenous compounds in lactic acid curd. It has insoluble and water-soluble proteins, as well as peptides, amino acids, amines and other nitrogenous compounds [5].

Low-molecular protein fractions are absorbed on the surface of high-molecular fractions giving them higher stability in water solutions and contributing to binding of water, swelling, and in some cases (of certain fraction ratios) the transformation of protein into solute state. However, in most cases the strengthening of the bond between protein and water "capsule" is necessary for the complete dissolution of protein.

The action of organic acid salts is determined by their adsorption on the surface of protein. The anions of polybasic acids have great adsorb ability and bind with curd proteins giving them negative charge [16, 18…20].

The salts with polyvalent anions and univalent cations in solution act as alkalis. When fully substituted salts are added to the protein base, the exchange reactions take place between them and proteins, as well as between their break down products and mineral salts. As a result, freely soluble protein salts with univalent cations form in the mixture. The process is marked by the increase of the protein base's pH and the protein's transition into liquid state, which contributes to its stability during high temperature heat processing. The protein base from fat-free lactic acid curd, which was heat processed in the presence of alkaline or basic salts, has alkaline smack, which considerably worsens its quality. That is why medium and weak-acid salts of acids should be used in the snack products technology [4, 5, 21, 22].

For the substantiation of choosing a melting salt two basic physical-chemical processes taking place due to the breaking down of CCPC caused by Na^+ ions of the organic acid salt and thermal processing in the temperature interval 80 ± 2^0C were investigated: the decalcification, which was determined by complexometric titration [23…25] with the use of Trilon B and MX metal chrome indicator ($C_8H_8N_6O_6$) (Figure 4.4), and the peptization of protein micelles, which was calculated as the ratio of soluble protein to the total (Table 4.1) in the protein base of the snack paste [26].

The investigation of the decalcification of the protein base (Figure 4.4) has established that the increase of a melting salt concentration within 1…3% provides for the transition of calcium into ion form: for trisodiumpolyphosphate - from 40 to 90 mg/%, sodium citrate – from 21 to 62 mg/%, for the mixture of sodium citrate and sodium bicarbonate in proportions 3:1,4:1, 5:1 – from 38 to 86 mg/%, from 36 to 84 mg/%, from 30 to 71 mg/% of ion calcium in the protein base respectively [27].

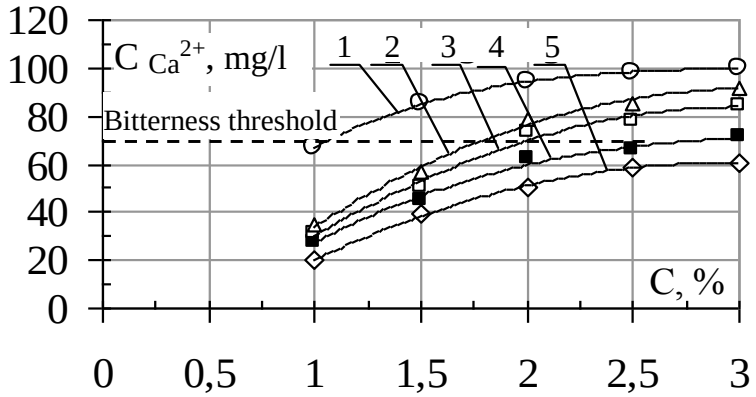


Figure 4.4. |The dependence of Ca $^{2+}$ ion concentration in the protein base on a melting salt content: 1 – trisodiumpoly-phosphate; 2, 3, 4 – sodium citrate+sodium bicarbonate in ratios 3:1, 4:1, 5:1 respectively; 5 – sodium citrate

It is worth mentioning that trinsodiumphosphate provides for ~10% greater protein hydration than sodium citrate, at already at 1±0,1% concentration, which corresponds to pH 5,8±0,2, it gives the protein base soap (alkaline) smack and bitter aftertaste (Table 4.1), while sodium citrate similarly affects the flavor at 3,5±0,2% concentration. The bitterness was caused by ions of calcium, the number of which during the ion exchange between Na^{+} and Ca^{+2} was ~30% greater in the protein base than during the interaction with sodium citrate [4, 5, 21, 27].

Due to peptization, casein micelles break down to smaller size increasing the protein surface and the number of hydrophilic groups, which contact with water. Further immobilization of free moisture takes place. The amount of bound water increases, while the amount of free moisture decreases (Figure 4.12).

Table 4.1 – The effect of melting salt on the peptization of protein of the protein base

Concentration, %	Peptization, %				
	Trisodium-polyphosphate	Sodium citrate	Sodium citrate and bicarbonate in proportion		
			3:1	4:1	5:1
0.5	18.1 ±1.2	14.6 ±1.1	19.5 ±1.2	18.3 ±1.2	17.5 ±1.2
1.0	25.4 ±1.3	23.1 ±1.3	28.0 ±1.3	26.7 ±1.3	25.0 ±1.3
1.5	52.0 ±1.5	46.8 ±1.4	55.1 ±1.5	54.4 ±1.5	53.1 ±1.5
2.0	62.3 ±1.5	50.4 ±1.5	65.3 ±1.5	64.9 ±1.5	63.3 ±1.5
2.5	64.8 ±1.6	62.5 ±1.5	68.4 ±1.6	65.8 ±1.6	65.0 ±1.6
3.0	68.6 ±1.7	64.3 ±1.6	72.4 ±1.8	70.5 ±1.8	69.4 ±1.8

The sensory evaluation of the effect of the degree of protein decalcification on organoleptic indices on a five-point scale (Table 4.2) has shown that the flavor qualities of the protein base are better, when the 5:1 sodium citrate and bicarbonate mixture is used.

Table 4.2 – The dependence of the organoleptic evaluation of the snack pastes' protein base on the calcium ion (Ca^{+2}) content, when the concentration of a melting salts is 2,0±0,1%

Melting salt		Organoleptic evaluation based on importance, points					
		appearance	consistency	color	aroma	flavor	Total
		0.12	0.25	0.1	0.2	0.33	
Trisodiumpolyphosphate		0.46	1.20	0.30	0.82	0.81	3.56
Sodium citrate		0.48	1.05	0.30	0.92	1.38	4.33
Sodium citrate and sodium bicarbonate in proportion:	3:1	0.48	1.15	0.30	0.85	1.18	3.96
	4:1	0.49	1.13	0.30	0.90	1.26	3.99
	5:1	0.50	1.20	0.30	0.96	1.54	4.55

The obtained results have formed the base for the substantiation of the technology of snack pastes production on the base of fat-free lactic acid curd. The protein base's active acidity is to be within pH 5.8…6.2 and the respective protein's MRC – 58…75%. These conditions are necessary to keep the protein from denaturation during thermal processing at 80 ± 2^0 C (Figure 4.1). Taking into consideration that the active acidity value of fat-free lactic acid curd, as a rule, fluctuates within 4.7…5.2, it is necessary to control the desired pH value by adding 0.4±0.1% of sodium bicarbonate and 2±0.2% of sodium citrate to the total of the components of the snack paste's protein base.

To determine the rational concentrations of sodium bicarbonate as a corrector of active acidity and sodium citrate as a melting salt, the investigation of protein's MRC was performed in two stages: the protein base's pH was shifted towards neutral by one of the reagents while fixing the other.

At the first stage of the investigation to determine the sodium bicarbonate's effect on protein's MRC kinetics, the protein base's pH was shifted towards neutral to 6.5±0.2 by adding the solution with 0.0…3.0% sodium concentration while fixing the concentration of sodium bicarbonate within: 0.3%, 0.4%, 0.5%, 0.6% (Figure 4.5).

Due to hydrolysis, 0.3% concentration of sodium bicarbonate provides for 54% MRC of the protein base; 0.4% concentration – 72%; 0.5% concentration – 88%.

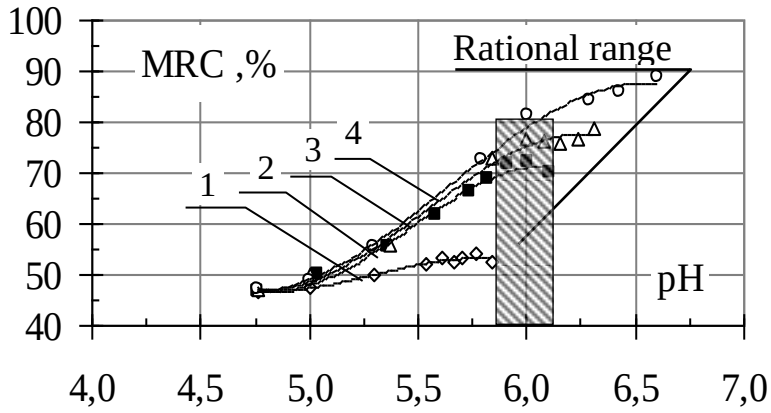


Figure 4.5. The dependence of the protein base's MRC on active acidity at sodium bicarbonate concentration: 1 – 0.3%, 2 – 0.4%;3 – 0.5%; 4 – 0.6%

The protein base attains the rational MRC value relative to thermal stability, when 0.4…0.5% of sodium bicarbonate is added (Figure 4.1). In this case the active acidity value increases to pH 6.2±0.1, and the protein base's MRC increases to 75±2%.

Thus, this concentration of sodium bicarbonate positively affects the process of hydration during the preparation of the protein base for thermal processing (Figure 4.6).

The increase of hydration of protein during shifting of pH in alkaline direction by sodium bicarbonate may be explained by the chart of ion exchange (Figure 4.6), due to which its hydrophilic ability increases, CCPC is breaking down, and protein micelles' sizes diminish [20].

This reaction confirms the role of cations and anions in the ion exchange in the protein base of lactic acid curd, and in the protein's pH and MRC increase at the same time.

The sodium bicarbonate's anion displaces calcium from the micelle chain and, by adsorptionally binding with casein, increases its negative charge. At the same time the mixture's pH shifts in the alkaline direction, and the isoelectric point shifts towards acid. As a result, casein increases its buffer capacity, swells during the aging of protein base, and keeps its aggregate equilibrium. The cation of sodium joining through the serinephosphate group the casein molecule, which due to the loss of the cation of calcium, had got the negative charge, forms easily soluble protein salt – sodium caseinate, which increases protein's general solubility.

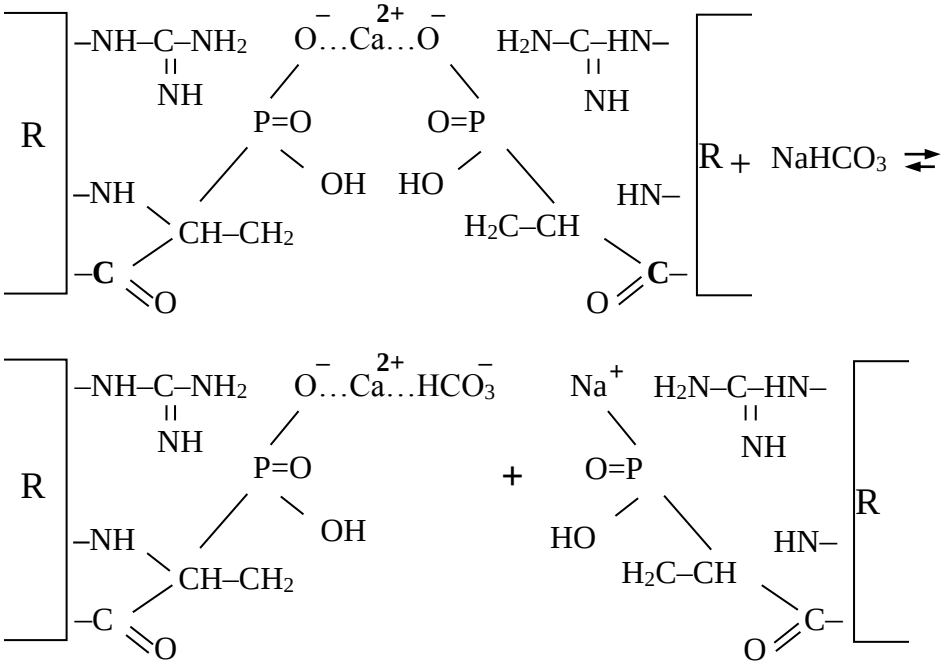


Figure 4.6. The ion exchange, when sodium bicarbonate is added to the protein base of snack pastes

At the second stage of the investigation (Figure 4.7) to determine the effect of sodium citrate on protein's MRC, the protein base's pH was shifted towards

neutral to 6.5±0.2 by adding the solution with 0.0…1.1% sodium bicarbonate concentration while fixing the concentration of sodium citrate within: 1.0±0.1%, 2.0±0.1%, 3.0±0.1%.

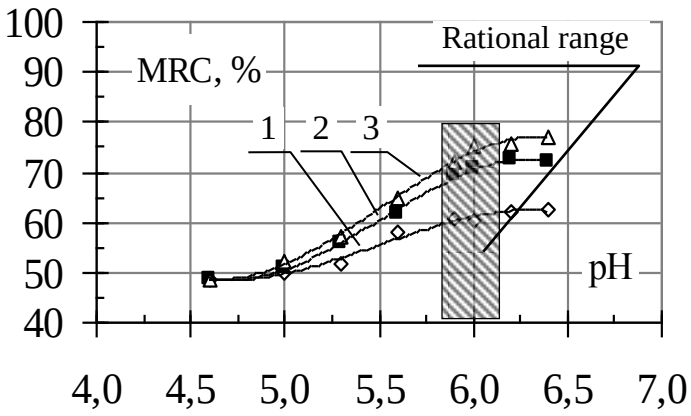


Figure. 4.7. The dependence of the protein base's MRC on active acidity at sodium citrate concentration: 1.0±0.1%, 2.0±0.1%, 3.0±0.1%.

1.0±0.1% concentration of sodium citrate provides for 70±1% MRC of the protein base; 2.0±0.1% concentration –75±2%, 3.0±0,1% concentration –78±2%.

The analysis of the graphs has shown that the increase of the sodium citrate concentration from 2±0.1 to 3±0.1% causes an insignificant 4% increase of MRC. However, at the same time the active acidity grows significantly to pH 6.2…2.7, and the flavor deteriorates.

The further increase of the active acidity takes place due to the hydrolysis of sodium citrate (Figure 4.8), which provides for the ion exchange, the further breaking of CCPC (Figure 4.9) augmenting the protein's buffer capacity [20, 27].

$$1–\ C_6H_5Na_3O_7+H_2O\rightarrow C_6H_6Na_2O_7+NaOH$$

$$2–\ C_6H_6Na_2O_7+H_2O\rightarrow C_6H_7NaO_7+NaOH$$

$$3–\ C_6H_7NaO_7+H_2O\rightarrow \underbrace{C_6H_8O_7}_{\text{Citric acid}}+NaOH$$

Figure. 4.8. The hydrolysis of sodium citrate (1,2,3 – stages of hydrolysis)

It has been established that the rational active acidity value, which ensures the necessary conditions for the protein hydration, must be within pH 5.9…6.0 (Figures 4.5, 4.7).

A powerful anion, adsorptionally binding with paracasein, forms the soluble salt of casein as a result of ion exchange caused by sodium citrate (Figure 4.9), increases casein's negative charge, due to which the protein increases its hydrophilic capability, swells during the aging of the protein base, and keeps its aggregate equilibrium. That is why proteins withstand a long period of heating at 80 ± 2^0C during thermal processing and do not denature [4, 20, 22, 28]. This pattern of ion exchange explains the increases of hydration of protein, when pH is shifted by sodium citrate, which causes the breaking down of CCPC, decrease of micelles' size, and increase of protein's hydrophilic capability [20].

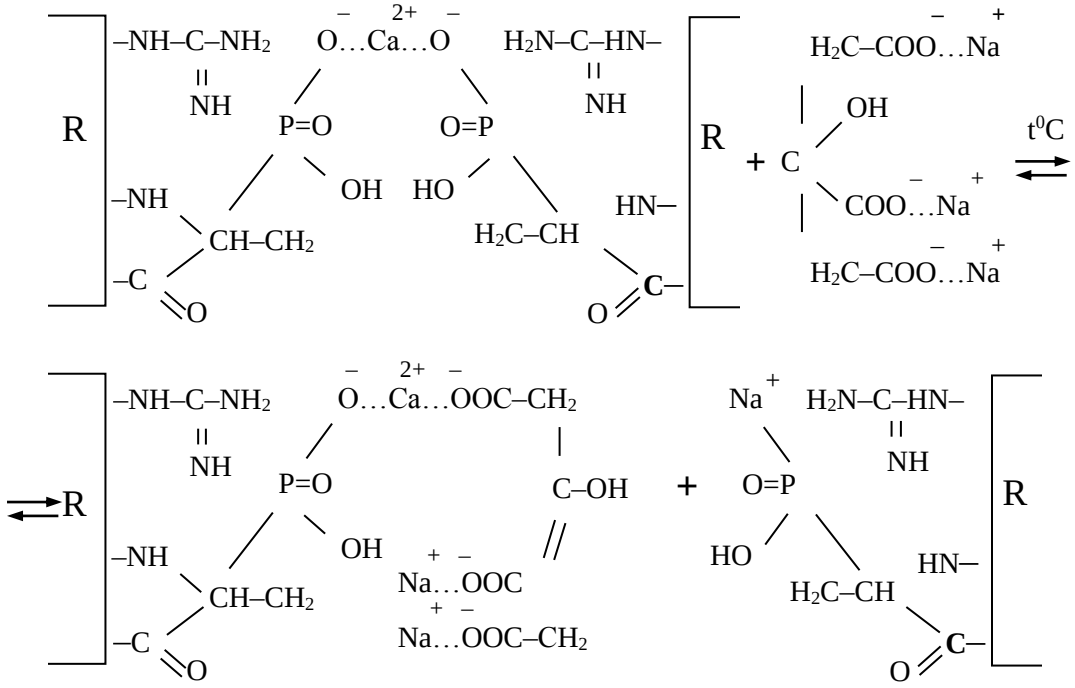


Figure 4.9. The ion exchange, when sodium citrate is added to the protein base of snack pastes

The research of the MRC of the protein base with different sodium citrate concentrations has been performed to determine the rational aging time.

It has been established (Figure 4.10) that during the aging of the snack pastes' protein base the MRC grows during the first $(28\pm2)\times60$ sec and depending on different sodium citrate concentrations: 1.0±0.1%, 2.0±0.1%, 3.0±0.1% attains the values: 64±2%, 75±2%, 77±2%. respectively. During the next $(28\pm2)\times60$ sec the MRC only grows 3.0±0.5%, probably due to the protein's decreased activity, because of MRC saturation.

Thus, the mixture with rational concentrations of 0.4±0.1% sodium bicarbonate as pH corrector and 2±02% sodium citrate as melting salt will provide for the protein base's 75±2% MRC increase after having been aged during

(28±2)×60 s, which will allow to raise its thermal stability during thermal processing to 95±2^{0}C (Figure 4.1).

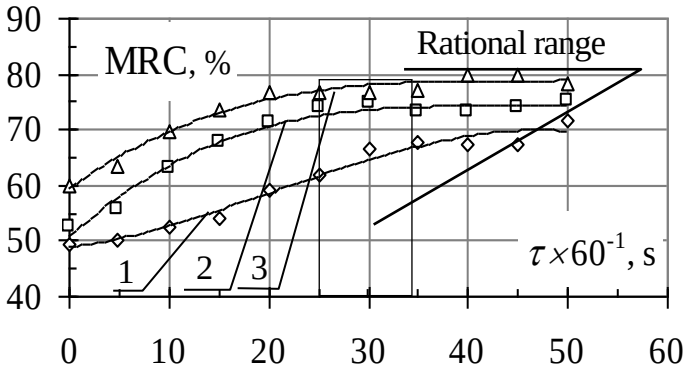


Figure. 4.10. The dependence of MRC on the aging duration of the protein base with 0.4% sodium bicarbonate concentration and sodium citrate, %: 1 – 1.0; 2 – 2.0; 3 – 3.0

Water is the main component of most products, which determines their commodity-processing characteristics (consistency, structure, succulence), their organoleptic indices, as well as their shelf life [29].

Due to their structural bonds it is characterized by various properties, availability, which lets divide it according to these characteristics into free and bound. That is why along with such characteristic as general moisture, food technology stresses other important indices of bound moisture, MRC. The ration between free and bound moisture is often the dominant index, which characterizes the technological processing, commodity, and microbiological stability of products.

Protein products, including the snack paste, contain water in various forms. Part of the moisture is represented by free water, and the other part by the so-called "bound water." The main biological molecules - nucleic acids, proteins, lipids are present in the mixture of the model paste in hydrated state, i.e. surrounded by a dense layer of water molecules. Biomolecules and water form a unique system, which cannot be divided into components without breaking its essence [28, 29…31].

Bound water tightly held by various components of food products due to chemical and physical binding is always present close to a dissolved nonaqueous component. It has reduced molecular mobility and other properties characteristic of free water (cannot be a solvent, cannot move separately in the system, but only with macromolecules at a certain sedimentation rate, viscosity, diffusion). It does not freeze even at –40^{0}C and differs from free water in structure [29]. Unfortunately, there is no distinct division between these two notions, because

bound water may have a wide “binding” spectrum [28, 29…31]. In food products it may be present in voids, pores, capillaries formed by a product body, as well as in sorbed state on the surface, hydrate and crystalline hydrate water, as well as other kinds of it. At the same time water molecules stay rather mobile, which is quite enough to observe them by the nuclear magnetic resonance (NMR) spin echo method [29, 34…37].

When using this method for the researched samples, the criterion chosen to characterize the forms of binding water in the protein base was the duration of spin-spin relaxation T_2, which is characteristic time of misphasing of magnetic moments (Figure 4.11) due to the formation of a local magnetic field by the closest neighbors, and which definines the degree of mobility of protons of hydrogen, and thus, the general molecular mobility of water in the protein base after its aging [34]. It was taken into consideration that NMR relaxation time depends on the chemical environment of the researched nuclei [36,38]. Thus, the rate of energy re-distribution in the spin system will be affected by spin-spin interaction and molecular mobility of water. So, T_2 in the experiment is characterized by the interaction of water with protein (binding energy). The spin echo method was chosen to determine the kinetics of the changes of the water dipole relaxation rate with the help of the NMR pulse device [34, 35, 37].

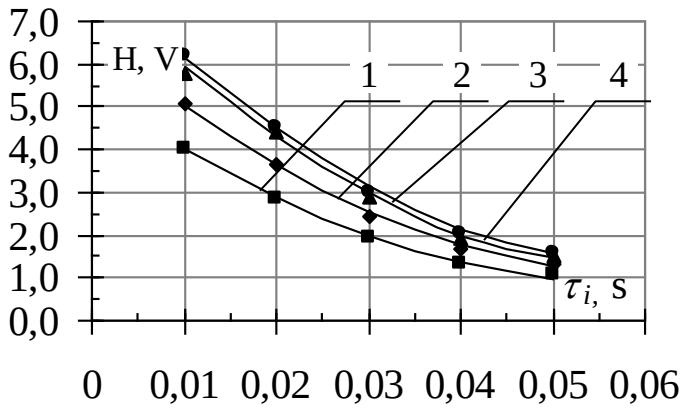


Figure 4.11 The dependence of the changes of echo signal’s amplitudes on τ_i interval between probe pulses in the snack pastes’ protein base with different sodium citrate content: 1 – 0%, 2 – 1.0%, 3 – 2.0%, 4 – 3.0%

After the processing of the experimental data on each researched sample we have found the dependence of the magnitudes of echo signal’s amplitudes (Figure 4.11) on τ_i interval between probe pulses at 0.4±0.05% sodium bicarbonate concentration and different concentrations of sodium citrate in the protein base.

The magnitudes of echo signal's amplitudes of the researched sample of the protein base without sodium citrate and the sample with 1.0±0.1% sodium citrate concentration differ by 1±0.1V; the samples with 1.0±0.1% and 2.0±0.1% sodium citrate differ by 1±0.1 V; the samples with 2.0±0.1% and 3.0±0.1% sodium citrate only differ by 0.25±0.05 V. This indicates that the further increase of the sodium citrate concentration over 2.0±0.1% does not considerably affect the amplitude.

After the mathematical processing of the results of the amplitude measurements [36, 38] the time of spin-spin relaxation T_2 depending on the sodium citrate concentration in the snack pastes' protein base was determined (Figure 4.12).

It has been established that the dependence of T_2 on the sodium citrate concentration within 1.0…3.0% is a smooth gradual curve (Figure 4.12), which characterizes the tendency towards the decrease of T_2, when the concentration of sodium citrate in the protein base is increased. It may be explained by the growing MRC of protein due to the ion exchange, which causes the reduction of the amount of "free" water in the snack pastes' protein base.

The graph in Figure 4.12 shows that when the sodium citrate concentration is increased within 0% to1.0±0.1%, the duration of spin-spin relaxation of water dipole in the snack pastes' protein base decreases by 0.007 sec; when it is increased within 1.0±0.1% to 2.0±0.1%, the duration decreases by 0.004 sec; when it is increased within 2.0±0.1% to 3.0±0.1%, the duration decreases by 0.002 sec. This means that we have established the tendency towards the decrease of molecular mobility and the increase of the content water bound by the protein with heightened sodium citrate content in the snack pastes' protein base.

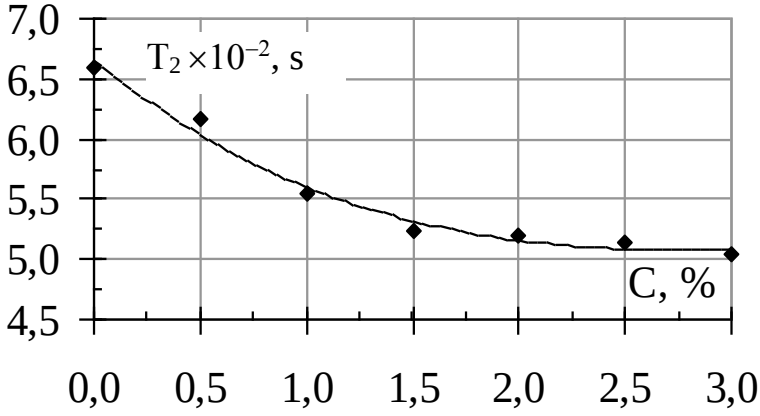


Figure 4.12. The dependence of the duration of spin-spin relaxation of water dipole in the snack pastes' protein base on sodium citrate concentration

It has been experimentally proven that the dependence of T_2 on the sodium citrate concentration within 1.0…3.0% is a smooth gradual curve (Figure 4.12)

with a sharp decrease within the interval of 0…2% sodium citrate concentration. It marks the tendency towards the decrease of T_2, when the concentration of sodium citrate in the protein base is increased. It may be explained by the growing hydration of protein and its water-binding activity due to the ion exchange, which causes the reduction of the amount of "free" water in the protein base. So, research has confirmed that 0…2% concentration of sodium citrate is rational, and its further increase in the snack pastes' protein base will not considerably affect the amount of bound water.

The X-ray analysis of the snack pastes' structural order (Figure 4.13) was performed with DRON-3 stationary X-ray machine [39]. The X-ray diffraction patterns of samples #1, #2, #3 show that they are characterized by amorphous X-ray spectrum, which covers the area of angles 2θ from 14^0…36^0.

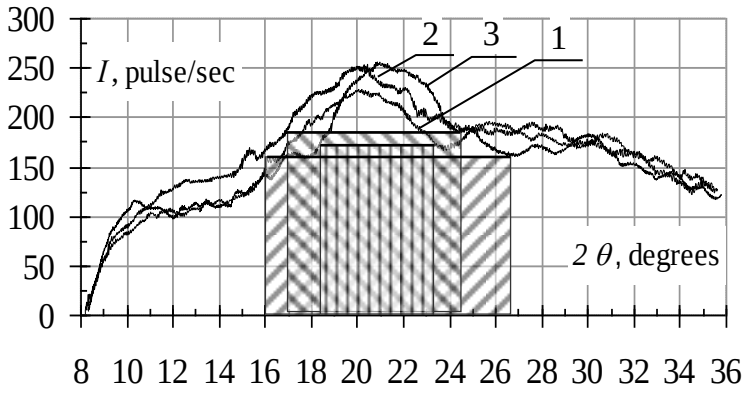


Figure 4.13. The dependence of diffraction line intensity on angle of reflection in the snack pastes' protein base with sodium citrate concentration: 1 – 1.0±0.1%; 2 – 2.0±0.1%; 3–3.0±0.1%

The maximum of diffraction line intensity is observed at the angle of reflection $2\theta=20.5^0$, which corresponds to interplanar spacing d=4.30Å calculated by Wolf-Bregg equation [40, 42].

The diffraction maximum on the "liquid-type" lines may point out the particles' tendency towards ordering. The higher orderliness is observed in samples #2 and #3 at 2% and 3% concentration of sodium citrate in the snack pastes' protein base respectively. Samples #2 and #3 have a more distinct diffraction maximum. Besides, the diffraction pattern shows an additional maximum with d=3.49Å.

The increase of the intensity of the basic maximum to d=4.33Å was observed in the samples after natural drying in the open air. It may the proof of the increased degree of structure order due the reduction of the diffusion background in the samples due to the loss of weakly bound water. These effects are more pronounced in samples #2 (Figure 4.14) and #3, whose integral half-widths of diffraction line (shaded area) are

smaller and are 0.108 and 0.107 of radian respectively. The area under the curve is proportional to the number of particles, which cause this reflection.

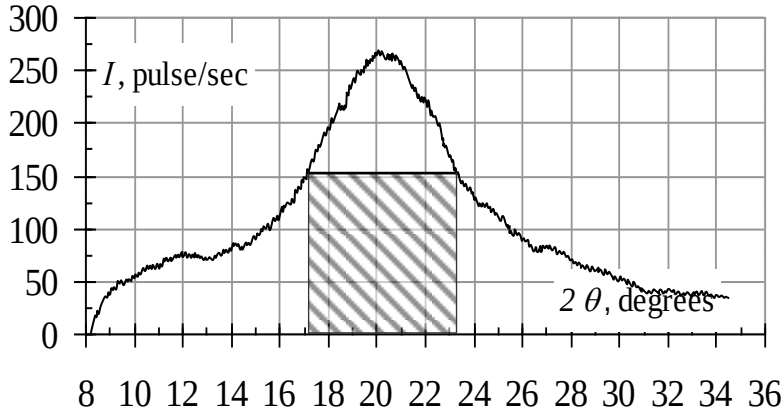


Figure 4.14. The dependency of diffraction line intensity on angle of reflection in the snack pastes' protein base after natural drying

The increase of the intensity of the basic maximum to d=4.33Å was observed in the samples after natural drying in the open air. It may the proof of the increased degree of structure order due the reduction of the diffusion background in the samples due to the loss of weakly bound water. These effects are more pronounced in samples #2 (Figure 4.14) and #3, whose integral half-widths of diffraction line (shaded area) are smaller and are 0.108 and 0.107 of radian respectively. The area under the curve is proportional to the number of particles, which cause this reflection.

The effective average size of the particles was estimated by the diffraction line half-width [41, 42]. We calculated the following sizes of particles in the samples: Sample #1 - D=12Å, Sample #2 - D=13.3Å, Sample # 3 - D=13.6Å. This means that the particle sizes of different samples differ insignificantly by 1.1…1.3 Å. Thus, they may be considered of similar size.

If we assume that the snack pastes' protein base consists of very thin packs of 2, 3, 4 layers instead of single layers, then it will be possible to investigate the accuracy of the experimental curve by comparing it the calculated one (Figure 4.15).

Absolute units were used for the intensity I_{ref} . Thus, the research could compare not only the shape, but also the height of the intensity curves of the samples of the snack pastes' protein base with different concentrations of sodium citrate. The interplanar atomic spacing may be considered a substance's "ID card."

The calculations show that the shape and the height of the intensity curve for N=3 and x=1 coincides well with the experimental curve (Figure 4.15). The calculated particle size in the 3-layer pack is similar to the particle size determined experimentally for sample #2: 3×4.30=13 Å.

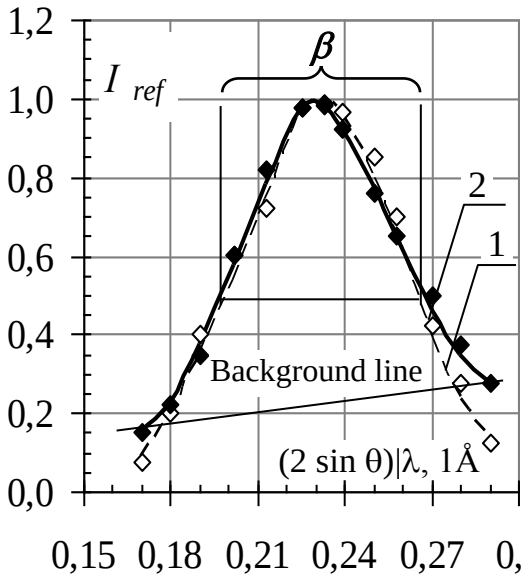


Figure 4.15. The dependency of diffraction line intensity on angle of reflection: 1 – calculated**,** 2 – experimental

Thus, it may be assumed that the snack pastes' protein base consists of the particles not more than 13Å thick randomly oriented along the normal to atomic reflection planes.

The experimental research of the snack pastes' protein base has established that their pattern order is affected by the sodium citrate concentration. By the diffraction line half-width and the height of the maximum we can state that samples #2 and #3 have a more orderly structure compared to sample #1, which confirms the sodium citrate concentration within 2±0.2% determined during the previous research.

Thus, the X-ray researches of the structure order have confirmed the previous research findings (Figure 4.7, 4.12) that the rational sodium bicarbonate concentration in the snack pastes' protein base is 0.4±0.1%, and sodium citrate concentration - 2±0.2%, which provide for the necessary thermal processing conditions.

4.1.3. Selecting and Substantiating the Fat Component Concentration

It is known, that the main fat component used to produce snack pastes for the modern food market is mostly butterfat, which is part of hard cheeses – protein base, as well as cream and butter. Butterfat gave the snacks cream flavor and consistency [4, 5].

However, the substantial reduction of milk production and its high cost in Ukraine created the deficit of butterfat, which is used to produce a wide range of dairy products. In addition, the new market economic conditions forced producers

to search for its less deficient cheaper, and more biologically and nutritionally valuable substitute. This has lead to a wide use of different fats and their compositions for partial or total substitution of butterfat. The chief requirement to substituting butterfat by vegetable oil is raising nutritional value and organoleptic indices of dairy products with possibly lower cholesterol.

Vegetable fats contain many vitally important essential polyunsaturated fatty acids, as well as vitamin E (tocopherols), which plays an important part in human organism [2, 3]. Table 4.3 shows butterfat's and some vegetable oils' physical-chemical properties according to Ukrainian scien tists [43, 45].

The vegetable substitute's flavor and aroma are to imitate butterfat's characteristic flavor and aroma or be neutral and stable during storage of finished products.

Table 4.3 – The physical-chemical properties of butterfat and some vegetable oils

Name	Temperature, °C		Saponification number	Iodine number
	melting	fixing		
Butterfat	28...33	18...23	220...234	28…45
Sunflower oil	—	-16...-19	186...194	119…145
Corn oil	—	-10...-20	187...190	111…113

The use of purified deodorized sunflower oil as fat component allows not only lower the cost and raise productivity, but also enlarge the product assortment, manufacture low cholesterol or cholesterol-free products, balance their saturated and polyunsaturated fats content.

It is known, that butterfat has extremely little content of essential acids: 1.5…4.4% of linoleic acid, 0.2…2.1% of linolenic acid, while sunflower oil contains up to ~60% of linoleic acid [43, 44].

According to the author's data [46], the difference in viscosity of different deodorized purified oils is insignificant and is $(1.2\pm0.2)\cdot10^{-3}$ Pa·s within the temperature range of $90\ldots70^0$ C, and $(2.5\pm0.1)\cdot10^{-3}$ Pa·s within the temperature range of $50\ldots30^0$ C.

To determine the rational concentration of oil during its emulsification into the snack pastes' protein base the investigation of dynamic viscosity was performed with different contents of sunflower oil (Figure 4.16) and emulsifying capability of protein base (Figure 4.17).

The research of temperature's effect on viscosity of the snack pastes' protein base with different contents of purified deodorized sunflower oil: 15; 20; 25% has

established that in the temperature range of 90…60^{0}C the dynamic viscosity is almost the same, i.e. ~50·10^{-3} Pa·s.

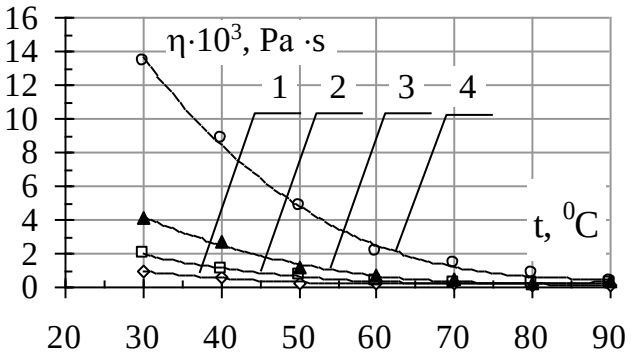


Figure 4.16. The dependence of viscosity of the snack pastes' protein base with sunflower oil content: 1 – 15%, 2 – 20%, 3 – 25%, 4 – 30% on temperature

The temperature decrease within 50…30^{0}C causes the increase of viscosity within 100…400·10^{-3} Pa·s. The increase of oil content in the protein base to 30±2% causes the considerable increase of viscosity within 75…200·10^{-3} Pa·s in the 90…60^{0}C temperature range, and the sharp increase of viscosity within 480…1350·10^{-3} Pa·s in the 50…30^{0}C temperature range, which may deteriorate the emulsification conditions.

The emulsification is known as an energy consuming process [47], so, it should be performed in the low viscosity zone. Thus, we accept 25±2% sunflower oil concentration at 30…40^{0}C with 280…400·10^{-3} Pa·s viscosity of the protein base as rational.

The emulsifying ability of the snack pastes' protein base (Figure 4.17) was investigated by determining the phase inversion point during emulsification by changing the concentration of one of the components of the protein base according to the standardized method [48, 49] at 35…40^{0}C, 77.6% humidity, mixing frequency of 25 c^{-1}.

It has been established that the sodium citrate concentration increase causes it to increase and reach maximal value of 50 volume units of oil at 2.0% concentration. The further increase of concentration causes the emulsification ability to decrease, probably, due to the increase of pH (Figure 4.17).

It has been established that the increase of the fat-free lactic acid curd content from 30% to 40% the emulsification ability of the protein base grows sharply. When the fat-free lactic acid curd content is increased to 50%, the emulsification ability slows down to 54 volume units due to the considerable augmentation of viscosity, which is confirmed by the previous researches (Figure 4.3).

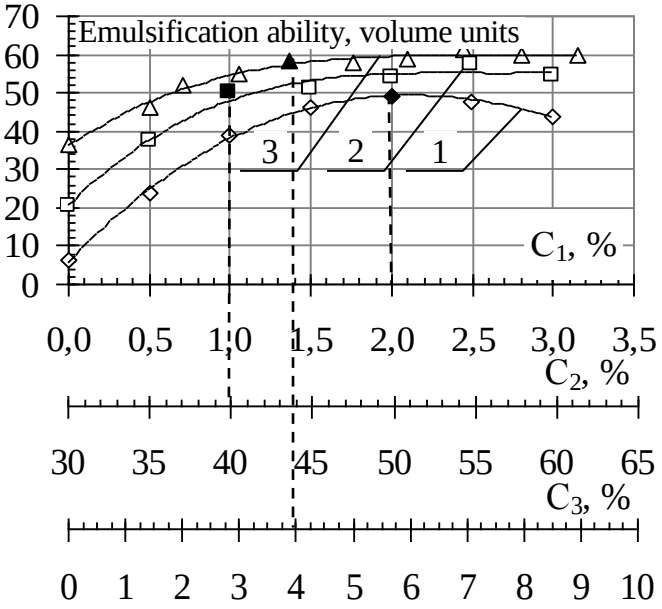


Figure. 4.17. The dependence of the emulsification ability the snack pastes' protein base on the concentration of the main components: 1 – sodium citrate (C_1); 2 – fat-free lactic acid curd (C_2); 3 – defatted dried milk (C_3)

The addition of up to 4.0% of defatted milk to the protein base as additional emulsifier contributes to the increase of the emulsification ability to 56 volume units of oil, when the content of fat-free lactic acid curd is 40%, probably due to the increase of the surfactant substances content.

An important index for the prolonged storage emulsification-type products is emulsion stability. It was determined by the content of broken down emulsion after a two-time centrifugation with in-between heating up to 90^0C. It has been established that the mass part of the unbroken phase of the model emulsion (Table 4.4) depends on fat content, concentration of protein–containing components of the protein base, and sodium citrate concentration.

The table shows that the model emulsions' stability of the snack pastes with 20…80% fat content is characterized by the mass part of the unbroken structure within 24…90% respectively, which depends on the content of the basic protein-containing components, oil, and the protein base's active acidity, which depends on the sodium citrate content.

The standardized method was used to build the graphs for the investigation of the emulsion stability before and after thermal processing (Figure 4.18, 4.19). This method's essence is in measuring the volume of fat and water phases, which separated from the total due to the emulsion break-down [50]. The analysis of the diagram has shown that before the thermal processing the model emulsion's aggregate stability is high. It is 96…98% and does not depend on the content of

protein-containing substances and oil within the researched concentrations (Figure 4.18). However, the kinetic stability is low. When the oil content in the model emulsion is 20±1%, dried milk content is 6,0±0,5%, and lactic acid curd content is30±2%, 40±2%, 50±3%, it is 30±2%, 65±2%, 78±2% respectively. The increase of the oil content from 20 to 80% increases the emulsion stability by 65% when the lactic acid curd concentration is 30%; by 31% when the lactic acid curd concentration is 40%; by 20% when the lactic acid curd concentration is 50%.

Table 4.4 – The stability indices of the model emulsion of the snack pastes

Component	Concentration, %	Mass part of the model emulsion, % at fat content, %			
		20	40	60	80
fat-free lactic acid curd	30	24	66	84	94
	40	60	83	86	96
	50	76	88	94	98
	60	78	90	96	98
Dried fat-free milk	0	38	63	76	88
	4	56	78	82	92
	6	60	83	86	96
	8	86	94	98	98
Sodium citrate	0	22	31	40	48
	1	42	58	64	81
	2	60	83	88	96
	3	62	80	86	94

It has been established that thermal processing at 80±2^{0}C contributes to almost 1.5 increase of the model snack paste emulsion's kinetic stability (Figure 4.19).

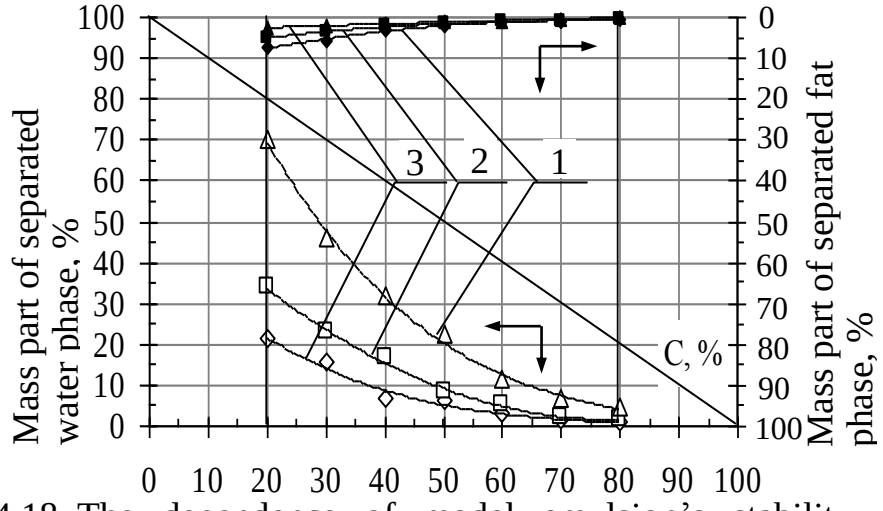


Figure 4.18. The dependence of model emulsion's stability on oil concentration before thermal processing with the fat-free lactic acid curd content, %: 1 – 30; 2 – 40; 3 – 50

After the thermal processing the stability of the emulsion containing 20±1% of oil increases from 30 to 70%, when the lactic acid curd content is 30±2%, from 65 to 84% when the lactic acid curd content is 40±2%, from 78 to 94% when the lactic acid curd content is 50±2%, probably due to the increased water binding by protein.

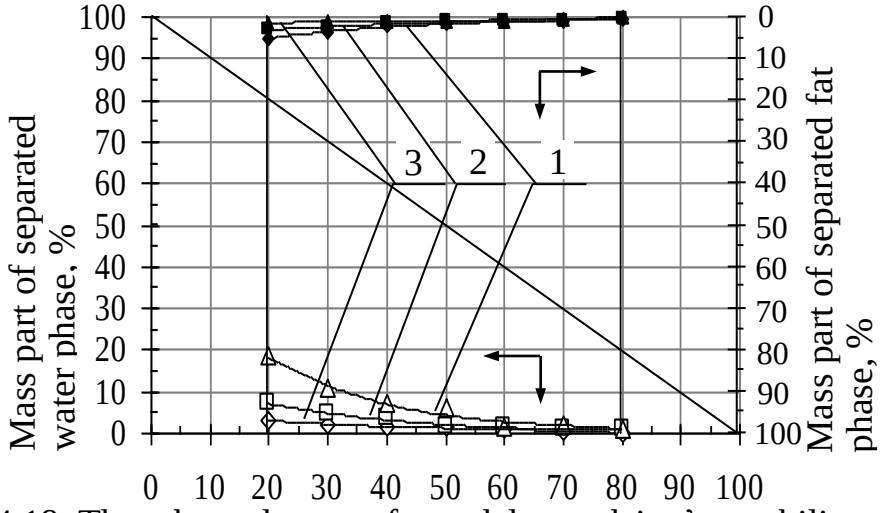


Figure 4.19. The dependence of model emulsion's stability on oil concentration after thermal processing with the fat-free lactic acid curd content, %: 1 – 30; 2 – 40; 3 – 50

Thus, the research has proved that the fat content of the model emulsion of snack pastes may be in a wide range from 20 to 60% keeping the aggregate stability. It is a valuable idea to add to the protein base 4±1% of dried milk, which increases the emulsification ability by 28±2 volume units when the lactic acid curd content is 28±2%. The 2±0,2% sodium citrate concentration has been confirmed as rational, since it provides for the greatest emulsification ability. Another factor proving for the high kinetic stability of the snack pastes' model emulsion besides thermal processing is the obligatory addition of a structure-former with high water-binding capability to the recipe composition.

The investigation of the changes in the microstructure of the snack pastes' model emulsion [51, 52] were aimed at visual confirmation of the qualitative changes taking place during the aging of the protein base (4.20, 4.21) and the changes in the microstructure of the model emulsion caused by sodium bicarbonate, sodium citrate, and thermal processing (4.22, 4.23).

On the microphotograph (blown up x1200) the structure of the fat-free lactic acid curd looks like net framework (Figure 4.20), formed by casein micelles (arrow 1 points at the aggregation of casein micelles, which form protein framework, arrow 2 points at the areas occupied by water phase).

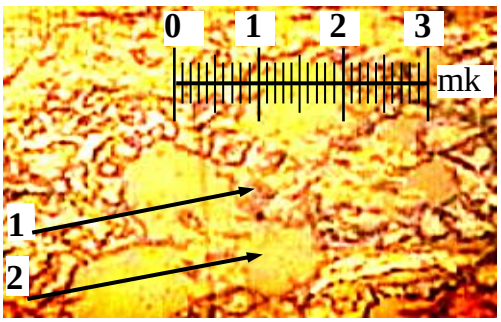
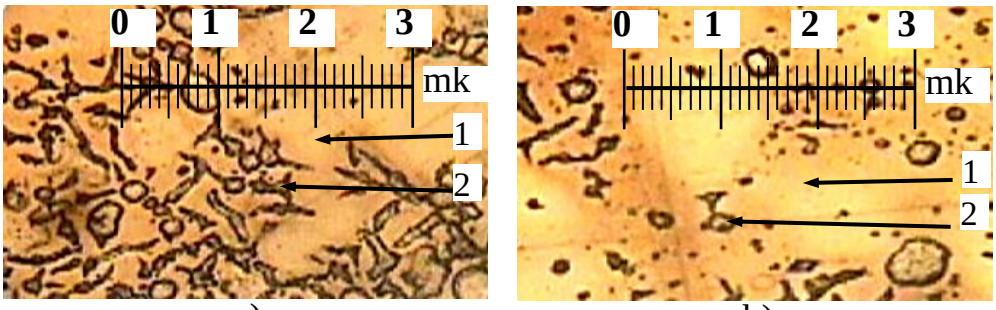


Figure 4.20. The microphotograph of the structure of the fat-free lactic acid curd before adding sodium citrate

During the additions of solutions: pH modifier - sodium bicarbonate and melting salt -sodium citrate and aging of the protein base during (28±2)×60 s the breaking down of the micellar structure of protein takes place (Figure 4.21) due to the exchange reaction, i.e. sodium citrate's Na^+ joining the casein molecule through the serinephosphate group (Figure 4.9). The casein molecule due to the loss of calcium cation has obtained the negative charge, which increases the whole protein's solubility. This is to say that sodium citrate, as well as sodium bicarbonate, participates in the exchange reaction further breaking the CCPC during the aging of the protein base.

Thus, due to the hydrolysis of sodium citrate during the aging of the protein base, the further breaking of "calcium bridges" takes place. This is confirmed by the micro-researches of the structure (Figure 4.21) before the emulsification and thermal processing. The sodium cation, which improves the protein solubility and the attachment of the powerful anion, joins paracasein in the micelle chains. This considerably increases the hydration and the solubility of protein due to the formed sodium citrate (Figure 4.9). The easily soluble citric acid salt prevents gluing of protein particles and increases its hydrophilic properties [5, 6, 19, 20].



a) b)

Figure 4.21. The microphotographs of the structure of the protein base with sodium bicarbonate and sodium citrate after aging: a – (10±2)×60 s; b – (28±2)×60 s

Thus, the microphotographs of the structure have confirmed that after adding sodium bicarbonate and sodium citrate to the protein base of snack pastes and aging during (28±2)×60 s (Figure 4.21 b) the microstructure goes through a significant change due to the additional binding of water after the relevant exchange reactions taking place in the protein base, its partial homogenization takes place and its uniformity increases.

In the microphotographs (Figure 4.21, a, b) arrow 1 points to the areas with uniform structure, arrow 2 points to the remains of the protein framework and casein micelles, which have formed this network.

The breaking of the calcium bridges, the corresponding pH value and the considerable hydrophilization of protein (Figure 4.5…4.9) cause the diminishing of micelles and the emergence of more hydrated submicelles of A, B, C type (Figure 1.2), as well as separate protein molecules and amino acids in the protein base. The protein suspension becomes more uniform.

After the emulsification of oil into the protein base and the thermal processing at 80±2^{0}C the emulsion forms (Figure 4.22, 4.23) from fat and water in the environment of solid-like highly hydrated protein.

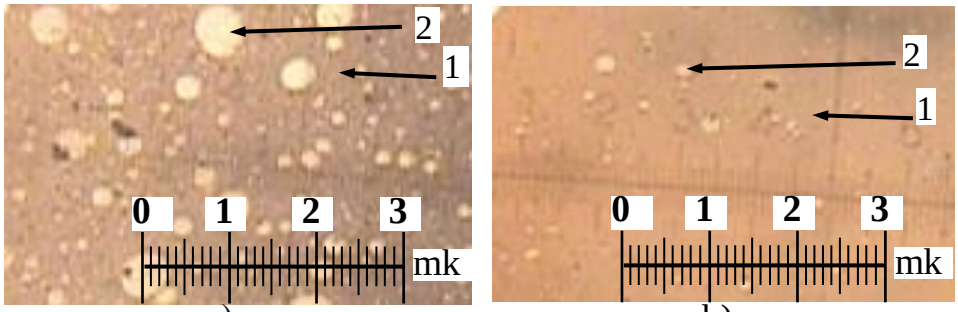
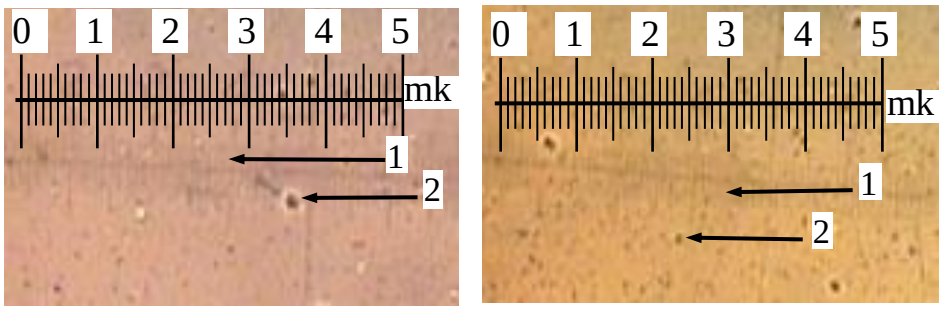


Figure 4.22. The microphotographs of the structure of the model emulsion of the snack pastes with sodium citrate concentrations: a – 1.0%; b – 1.5%

The microphotographs (Figure 4.22, a, b) have confirmed that 1.0±0.1%, 1.5±0.1% concentrations of sodium citrate in the model emulsion of the snack pastes cause forming the porous unbound structure (arrow 1 points to the areas with uniform structure, arrow 2 points to the areas with parts of unmelted protein). The model emulsion of the snack pastes has uniform structure (Figure 4.23) with properties characteristic of this product, when concentrations of sodium citrate are 2.0±0.1% and 3.0±0.1%.

The analysis of the microphotographs has shown that the microstructures of the model emulsion of the snack pastes with 2.0% and 3.0% sodium citrate

concentrations (Figure 4.23, a, b) are almost similar. Arrow 1 in the microphotographs points to the areas with the unform structure, arrow points to the areas with fat drops, which have appeared during its coalescence.



a) b)

Figure 4.23. The microphotographs of the structure of the model emulsion of the snack pastes with sodium citrate concentrations: a – 2.0%; b – 3.0%

The investigation of the system's model microstructure after thermal processing (Figure 4.22, 4.23) has confirmed that sodium bicarbonate as pH corrector and sodium citrate as melting salt break milk protein's structure, considerably affect the model emulsion's structure, and increase the peptization of protein component (Table 4.1).

Thus, it has been proved that effect of sodium bicarbonate and sodium citrate on raising pH of the snack pastes' protein base and the increase of its moisture-retaining and emulsification capabilities. It has also been proved that 0.4±01% concentration of sodium bicarbonate as pH corrector and 2±0.2% concentration of sodium citrate as melting salt provide for the necessary conditions of obtaining the snack pastes' model emulsion.

4.1.4. Substantiation of the choice of a structure-former.

The technological aspects of obtaining snack products with emulsion structure are based on creating emulsion systems, which are highly disperse, stable over a period of time, and are characterized by heightened digestion compared to the products, in which fat is present in non-emulsified state.

Due to a wide spectrum of chemical composition and ingredients' nature most of the combined products, which include snack pastes on the base of lactic acid curd, are complex systems with a unique inner structure and general physical-chemical properties. Specific food additives are introduced into recipes to fulfill a specific processing task to stabilize the structure, produce the proper consistency characteristic of this type of products and structural-mechanical properties.

The important aspect in the technology of emulsion-type products is stabilization of obtained emulsions. Stabilization (the attainment of set physical, physical-chemical and other characteristics, and their maintenance over a period of time) is fulfilled by adding substances, which increase strength, structural viscosity of adsorptional interfacial layers, shorten the duration of structure-forming. It is also fulfilled by changing the technological parameters of processing of a recipe mixture or a finished product, which affect the change in structural-mechanical propeties: viscosity, strength, elasticity, etc. [53…56].

It is the modern trend to use the systems performing the role of stabilizers of water and fat phases in the technology of emulsion-type paste snacks. The main requirements are the following:

- compatibility with disperse phase and disperse environment;
- ability to ensure preserving a product during storage without synerisis and fit for culinary processing;
- fitness of the product for culinary processing;
- controlled rate of structure-forming and ability to transform the system from clot to paste;
- ability to provide for the necessary product consistency;
- absence of allergic or toxic effects;
- low cost, easy availability.

Complex requirements to the functional properties of substances used separately or as ingredients of recipe compositions to stabilize emulsification products envisage such characteristics as fluidity, thixotropy, the degree and rate of swelling, absence of synerisis during production and storage, stability of rheological properties, etc.

Recently there has been a notable use of protein substances as emulsifiers and stabilizers of technological systems. They have assumed the especially dominant position with the achievements of modern science, which have made their assortment much wider and their sources much more available [28, 53, 54, 57]. Besides, protein structure-formers, such as gelatin, milk, egg, flour proteins, etc. are also added to recipes to ensure resistance against delamination in these products and provide for their stability over the necessary time duration. Polysaccharide structure-formers – starch, pectin, carrageenan, as well as sulfated polysaccharides, such as agar, agaroid, furcellaran, etc. are widely used as stabilizers, too [56, 58…61].

The main criteria of selecting the type of a structure-former in our research were safety for human organism, high moisture-retaining capability. We preferred to use natural structure-formers, which can be synthesized by living organisms and

decompose under natural conditions, i.e. are ecologically pure high-molecular food polymers, including gelatin, agar, agaroid, furcellaran, carrageenan [59-61].

Taking into consideration that gelatin jellies' processing temperature is rather low, i.e. 25…35^{0}C, in the technology of the snack pastes on the base of lactic acid curd we consider it rational to use the polysaccharide structure-formers, such as agar, agaroid, furcellaran, carrageenan, which have a wide complex of functional-technological properties and high activation temperature [27, 54-56, 58-61].

Agar, agaroid, and furcellaran are sulfated galactans of red marine algae, included in phytocolloid group. They are soluble in hot water, produce high viscosity colloidal solutions and strong jellies even at low (1…3%) concentrations. Their main carbohydrate ingredient is water-soluble galactan, which contains galactose (of D and L-family), 3.6-anhydrogalactose, sulfuric acid, bound to galactan by complex ester bond. Carrageenans comprise several types of family polysaccharides, including agaroid produced from Phyllophora and furcellaran produced from furcellaria.They have similar hydrogen framework, but differ iin content of 3.6-anhydrogalactose, the amount and distribution of sulfate [27, 58-61].

The investigations of the functional-technological properties of jellies with the use of polysaccharides were performed within 2.75 N strength of the analog "Khreshchatyk" paste. It has been established that the 2.75 N strength of jellies is provided for by 1.3±01% agar, which is the lowest concentration. To provide for this strength the solution needs almost 2 times more of furcellaran, and almost 3 times more of carrageenan and agaroid (Table 4.5).

The investigation of the duration of the structure formation of polysaccharide gels of similar strength, e.g. 2.75±0.1 N at 20±5^{0}C, have shown that 1.3±0.1% agar needs the shortest time for structure formation. Thus, at 20±5^{0}C 1.3±0.1% agar gels begin structure forming after 30×60 s, 3.0±0.2% furcellaran gels begin structure forming after 60×60 s, 4.0±0.3% agaroid gels and 4.5±0.3% carrageenan gels begin structure forming after 120×60 s. The fastest to form structure are agar gels at (180±3)×60 s (Table 4.5), the slowest are carrageenan gels at (260±5)×60 s, and 1.3±0.1% furcellaran, agaroid, carrageenan do not form structure at all at this temperature.

The investigations of the temperatures of the thermal processing of the gel solutions have shown that for 1.1…2.0% agar it is within 73…90^{0}C, for 2.2…3.5% furcellaran it is within 53…68^{0}C, for 3.3…4.5% agaroid it is within 48…60^{0}C, for carrageenan it is within 45…55^{0}C.

Table 4.5 –The functional-technological properties of polysaccharide gels

Properties	Concentration, %			
	agar	furcellaran	agaroid	carrageenan
	1.3±0.1	2.9±0.2	3.9±0.3	4.0±0.3
Strength, N	2.75±0.5			
Duration of structure formation $\times 60^{-1}$, s	180±3	210±5	240±5	260±8
Thermal processing temperature, ^{0}C	80±2	60±1	55±1	52±1
Thermal stability at 50±2^{0}C, s	600±10	360±8	200±5	50±5
at 25±2^{0}C, s	2000±8	1400±5	980±3	800±3

Thus, the analysis of the temperatures of the thermal processing of the polysaccharide gels (Table 4.5) has confirmed that for 1.3±0.1% agar the temperature is 80±2^{0}C and is practically similar to the temperature of the thermal processing of the snack pastes. Other structure-formers have much lower thermal processing temperatures: 2.9±0.2% furcellaran – 58±1^{0}C, 3.9±0.3% agaroid – 55±1^{0}C, 4.0±0.3% carrageenan – 52±1^{0}C.

The investigations of the thermal stability of the polysaccharide gels of concentrations providing for the similar strength (Table 4.5) have shown that agar is the most thermally stable. Its thermal stability at 50±2^{0}C is 600±10 s, furcellaran 's thermal stability is 360±8 s, agaroid’s thermal stability is 200±5 s, carrageenan’s thermal stability is 50±5. The lowering of the temperature down to 25±2^{0}C (cooling of the pastes) causes agar’s thermal stability to rise by 1400±8 s and reach 2000±8 s, furcellaran's thermal stability to rise by 1040±5 s and reach 1400±5 s, agaroid’s thermal stability to rise by 780±3 s and reach 980±3 s, carrageenan’s thermal stability to rise by 750±3 s and reach 800±3 s.

Thus, taking into consideration the kinetics of the different concentration gels’ strength, structure formation, thermal processing temperatures and thermal stability (Table 4.5), it has been proved that agar has better functional-technological properties at lower concentration.

The investigation of the temperature effect on the dynamic viscosity of the gels: agar, agaroid, furcellaran, carrageenan of the same1.3±0.1 % concentration (Figure 4.24) has shown that agaroid has the lowest viscosity, and carrageenan has the highest.

It has been established (Figure 4.24) that within 80 ± 2^0C interval of the snack pastes thermal processing the polysaccharide gels' viscosity is the following: $1.4\pm0.2\cdot10^{-3}$ Pa·s for agaroid, $2.5\pm0.2\cdot10^{-3}$ Pa·s for agar, $2.8\pm0.1\cdot10^{3}$ Pa·s for furcellaran, $3.7\pm0.2\cdot10^{-3}$ Pa·s for carrageenan.

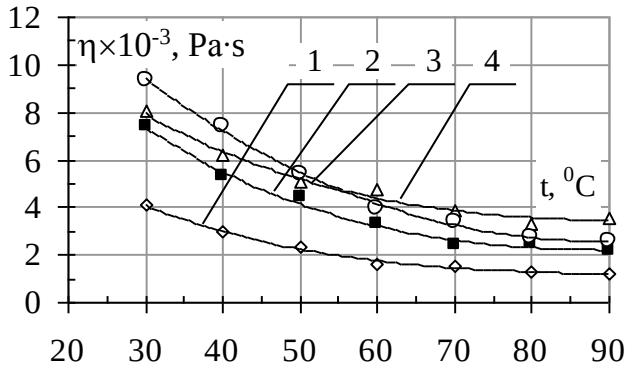


Figure 4.24. The dependence of dynamic viscosity on temperature at 1.3±0.1% gel concentration: 1 – agaroid, 2 – agar, 3 – carrageenan, 4 – furcellaran

At the concentration providing for the gels' structure formation (Figure 4.24) the viscosity of the structure-formers: agaroid, furcellaran, carrageenan will be much higher. This means that agar has lower viscosity under the same conditions and will have less effect on energy consumption during the technological process.

It is known that activation energy characterizes gel formation process rate, enthalpy characterizes strength, entropy characterizes structure order [27, 59].

We have built the graphs (Figure 4.25) of the dependence of the gel-formers' viscosity logarithm on the temperature $ln\ \eta = f((1/T)*1000)$ to calculate activation energy, enthalpy and entropy. The graphs have been built in semilogarithmic coordinates and have a distinct rectilinear character. We defined tgα of the angle of inclination of the lines, which characterizes the intensiveness of the change of the logarithmic curves in the diagram.

It has been established that the graphs have the breaking point at temperature 70 ± 5^0C, which characterizes the endothermic process, which goes on with a certain heat consumption within the temperature interval of $60\ldots70^0$C, probably, due to the breaking of physical-mechanical and physical-chemical bonds of water with protein during thermal processing.

Table 4.6 shows the calculations of the dependence of 1.3±0.1% gels' activation energy, enthalpy and entropy on temperature.

The investigations of the kinetics of dynamic viscosity of 1.3±0.1% agar, agaroid, furcellaran, carrageenan as possible structure-formers of snack pastes and the

calculations of activation energy, enthalpy and entropy (Table 4.6) have confirmed that agar has better functional characteristics compared to other polysaccharides.

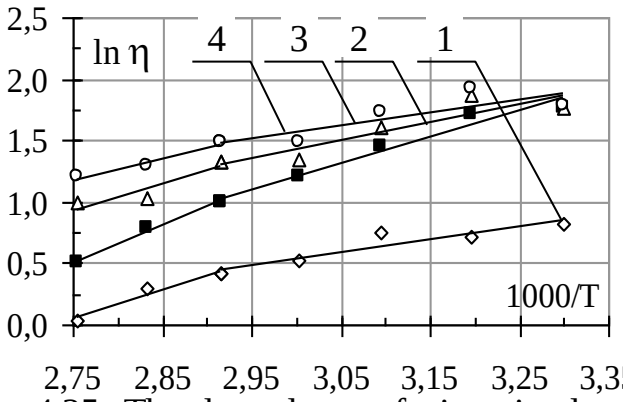


Figure 4.25. The dependence of viscosity logarithm on temperature at 1.3±0.1% concentration of the gels: 1 – agaroid, 2 – agar, 3 – furcellaran, 4 – carrageenan

Agaroid has the least viscosity at this concentration, high gel-forming ability, but also lower orderliness and strength of structure, which calls for higher concentrations of 3.9…4.2% for its use in the snack pastes' recipes.

Furcellaran and carrageenan also have lower structural orderliness and poor gel-forming ability, lesser strength, which also calls for higher 2.9…3.2% and 3.9…4.1% concentrations respectively. They have the highest dynamic viscosity among the researched, thus, they will negatively affect the energy consumption during the technological process. Besides, they are more expensive, thus, they lower the economic indices of the finished product.

Table 4.6 – The dependence of viscous flow activation energy, enthalpy and entropy on 1.3±0.1% gels' temperature.

Item	Attribute	Temperature, ^{0}C						
		30	40	50	60	70	80	90
Agar	Activation energy, kJ/kg	10.6±0.1	10.4±0.1	10.0±0.1	9.8±0.1	9.5±0.1	9.3±0.1	9.0±0.1
Agaroid		9.3±0.2	8.8±0.2	8.4±0.2	7.9±0.2	7.5±0.2	7.0±0.2	6.6±0.2
Furcellaran		11.0±0.3	10.8±0.3	10.5±0.3	10.4±0.3	10.2±0.3	9.9±0.3	9.7±0.3
Carrageenan		11.1±0.2	10.6±0.2	10.5±0.2	10.6±0.2	10.6±0.2	10.5±0.2	10.5±0.2
Agar	Enthalpy, kJ/kg	17.9±0.1	18.0±0.1	18.2±0.1	19.2±0.1	24.8±0.1	25.0±0.1	25.0±0.1
Agaroid		10.0±0.1	10.0±0.1	11.0±0.1	12.4±0.1	18.6±0.1	20.0±0.1	20.0±0.1
Furcellaran		12.3±0.1	12.3±0.1	12.4±0.1	13.0±0.1	17.4±0.1	17.6±0.1	17.6±0.1
Carrageenan		8.0±0.1	8.2±0.1	8.3±0.1	10.0±0.1	11.1±0.1	11.2±0.1	11.2±0.1
Agar	Entropy, kJ /^{0}K	0.12±0.1	0.21±0.1	0.29±0.1	0.38±0.1	0.46±0.1	0.54±0.1	0.62±0.1
Agaroid		0.13±0.1	0.22±0.1	0.3±0.1	0.39±0.1	0.48±0.1	0.56±0.1	0.63±0.1
Furcellaran		0.15±0.1	0.24±0.1	0.32±0.1	0.41±0.1	0.5±0.1	0.58±0.1	0.65±0.1
Carrageenan		0.18±0.1	0.26±0.1	0.35±0.1	0.44±0.1	0.52±0.1	0.61±0.1	0.68±0.1

Agar has lower viscosity than furcellaran and carrageenan, better structure orderliness, and lower viscous flow activation energy, i.e. a faster rate of the process. Besides, agar already attains greater strength than polysaccharides as soon as it reaches 1.3±0.1% concentration.

Thus, taking into consideration the polysaccharide gels' strength characteristics, viscous flow rate, structure orderliness and dynamic viscosity, and structure formers' concentrations, we may assume that within the working hypothesis agar is rational as a structure former for the model system of the snack pastes on the base of fat-free lactic acid curd. Adding it to the recipe will allow more possibilities of adjusting and controlling its structural-mechanical characteristics to achieve desired indices.

4.2. Investigating the Recipe Ingredients' Effect on the Technological Indices of the Snack Pastes' Model System

4.2.1 Changing Processing Temperature

The motor of the technological effect is the heating of the snack paste recipe mixture, whose protein component due to the mechanical effect during mixing, the ion exchange action of melting salt and the thermal effect transforms into soluble state, which provides for the formation of water-fat emulsion in the environment of hard highly hydrated protein.

Besides, the thermal processing temperature is an important parameter, which affects mass losses and the finished products quality due to water evaporation.

Considering the previous research of the snack pastes' model system on the base of fat-free lactic acid curd (Figure 4.17…4.19, 4.21…4.23), the effect of the components of the model systems on the thermal processing temperature (Figure 4.26…4.28) was disclosed during heating at 55…95^{0}C after its structure formation [14, 27, 46].

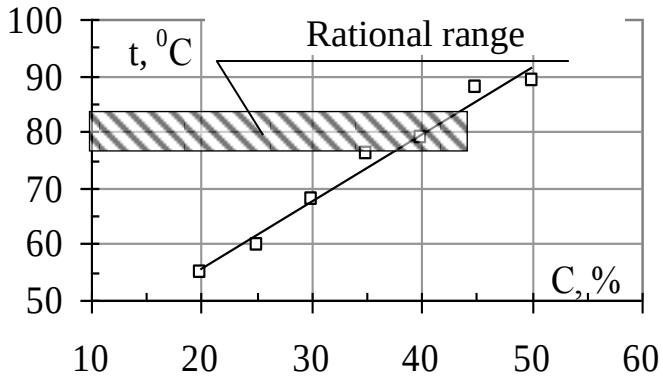


Figure 4.26. The dependence of the temperature of the thermal processing of the snack pastes' model system on fat-free lactic acid curd content

The main thermal processes, which go on in the pastes' model system in this temperature interval are characterized by the rising of the protein's hydration ability under the effect of the temperature, and by partial release of water weakly bound to protein. The research was performed by changing the concentration of one of the main recipe components while fixing the other within the rational values.

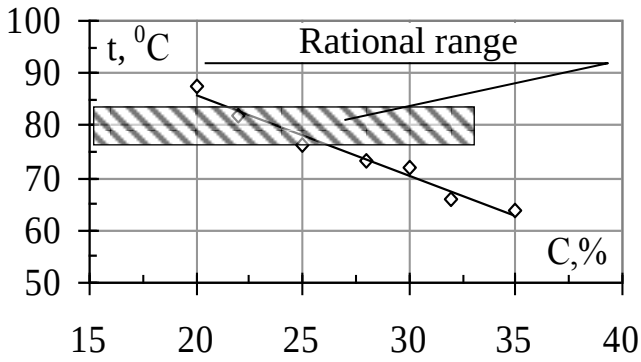


Figure 4.27. The dependence of the temperature of the technological processing of the snack pastes' model system on oil content

The 10% increase of the fat-free lactic acid curd content (Figure 4.26) raises the temperature of the thermal processing of the snack pastes by 12±3^{0}C; the 0.1% increase of the oil content (Figure 4.27) raises the temperature of the thermal processing of the snack pastes by 11±3^{0}C.

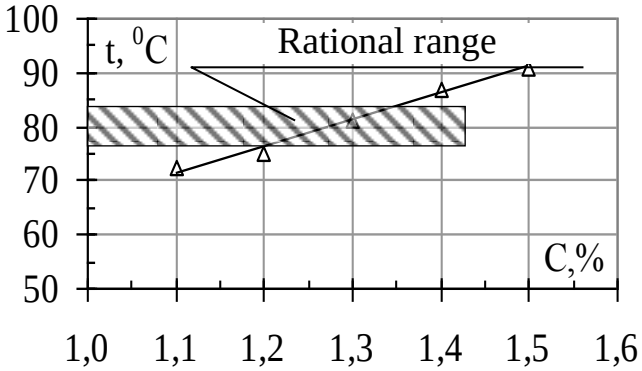


Figure 4.28. The dependence of the temperature of the technological processing of the snack pastes' model system on agar content

It is worth mentioning that the increase of the content of the recipe components of the model snack pastes: 20…50% increase of fat-free lactic acid curd content raises the thermal processing temperature from 55±2 to 90±2^{0}C, 1.1…1. 5% increase of agar content raises the thermal processing temperature from 73±2 to 90±2^{0}C, 20…35% increase of vegetable oil content lowers the thermal processing temperature from 85±2 to 63±2^{0}C.

On the average when the contents of the main components of the model system are within rational concentrations, the temperature of the thermal processing of the snack pastes' model system is 80±2^{0}C.

4.2.2 Changing duration of structure formation

The investigation of the effect of different recipe components on the duration of structure formation depending on each ingredient's contents (Figure 4.29, 4.30, 4.31) was performed at 20±2^{0}C with the help of static load [62] while fixing other main components' contents on the basis of the previous analytical and experimental researches (Figure 4.1…4.3, 4.16…4.19, 4.26).

It has been established that the increase of fat-free lactic acid curd content in the snack paste model system recipe from 30 to 50% shortens the structure formation duration at 20±2^{0}C from (120±2)×60 sec to (70±2)×60 sec (Figure 4.29).

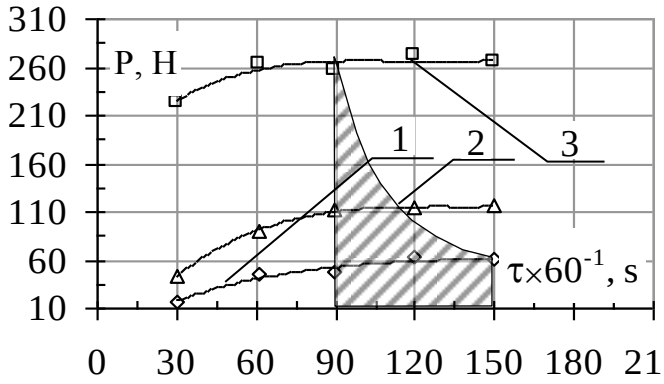


Figure 4.29. The dependence of the strength of the snack pastes' model system on the duration of structure formation with fat-free lactic acid curd content: 1 – 30%; 2 – 40%; 3 – 50%

The snack pastes' model system with 30% fat-free lactic acid curd content begins to structure after (100±2)×60 s; with 30% content - after (90±2)×60 s; with 50% content - after (70±2)×60 s.

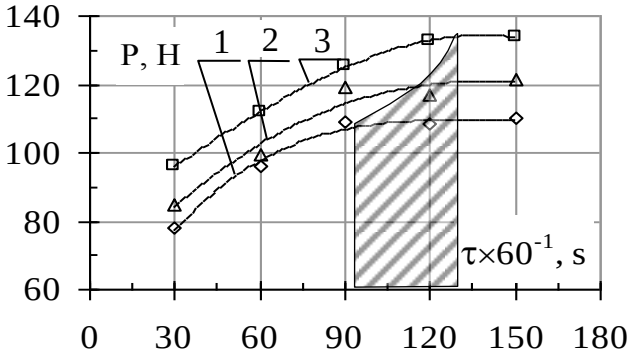


Figure 4.30. The dependence of the strength of the snack pastes' model system on the duration of structure formation with vegetable oil content: 1 – 20%, 2 – 5%, 3 – 30%

The increase of vegetable oil content within 20…30% causes the prolongation of structure formation of the snack pastes' model system from (100±2)×60 s to (120±2)×60 s (Figure 4.30).

The snack pastes' model system begins to structure with 20% vegetable oil content after (100±2)×60 s, 25% content – after (120±2)×60 s, 30% content – after (130±2)×60 s.

It has been established that adding agar to the model paste recipe considerably shortens the structure formation duration. The analysis of the graphs (Figure 4.13) has proved that at 20±2^{0}C he model system begins to structure after (90±2)×60 s if agar content is 1.1±0.1%, after (70±2)×60 s if agar content is 1.3±0.1%, after (50±2)×60 s if agar content is 1.5±0.1%.

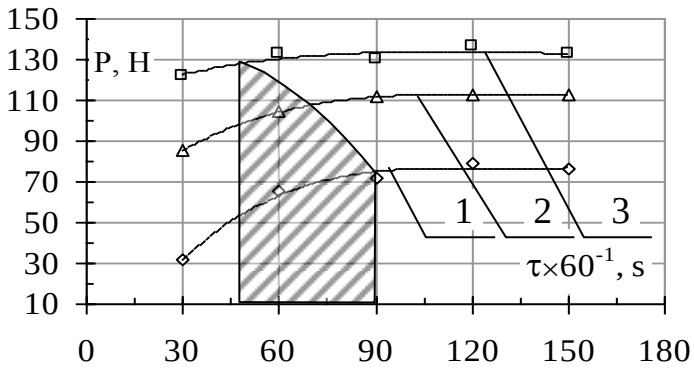


Figure 4.31. The dependence of the strength of the snack pastes' model system on the duration of structure formation with agar content: 1 – 1.1%, 2 – 1.3%, 3 – 1.5%

Thus, the main recipe components: 40±2% lactic acid curd, 1.3±0.1% agar, and 25±1% vegetable oil generally provide for (90±5)×60 s duration of the snack pastes' structure formation.

4.3 Substantiation of the Thermal Processing Parameters of Snack Pastes' Model System

4.3.1 Investigations of Processing Temperature and Duration

Most of the physical and chemical processes are accompanied by heat consumption (endothermic transformation) or release (exothermic transformation). Moreover, some of them may go in forward or reverse direction: melting-crystallization, boiling-condensation, polymorphic transformations. All these processes may be investigated while fixing mass and temperature changes [63…66].

The determination of kinetic parameters of endothermic processes (Figure 4.32), which take place along with changes of mass under non-isothermal conditions was

fulfilled with the help of differential thermogravimetry (DTG) and differential thermal analysis (DTA) using a derivatograph. Basic to these methods is the assumption that at constant rate of heating the values corresponding to the degree of mass change or heat consumption in the area of fixed beginning and maximal development of the process are proportional to the constant of transformation rate for each temperature value [66].

The experimental research of moisture losses, which have different forms of binding with protein, was carried out on the basis of the analysis of the mass change curves (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) at temperature (T) under the following conditions: the batch of the model paste was 180±2 mg, the rate of heating the samples was 5±1 degrees per 60 s under non-isothermal conditions, thermal junction was put in sample.

The peaks of DTG curve (Figure 4.32) witness the processes taking place due to the mass decrease. It may be assumed that the loss of the researched samples' mass is linked to release of water from the model system of the snack pastes due to thermal effect. The DTG and DTA curves are directed towards lowering temperature, i.e. we may assume that the process is endothermic.

Thus, it has been established that the decomposition process of all snack pastes' protein bases samples takes place endothermally in three stages with mass loss due to water vaporization. The curves show three endoeffects, whose positions are different for each sample depending on the main components contents [65, 66].

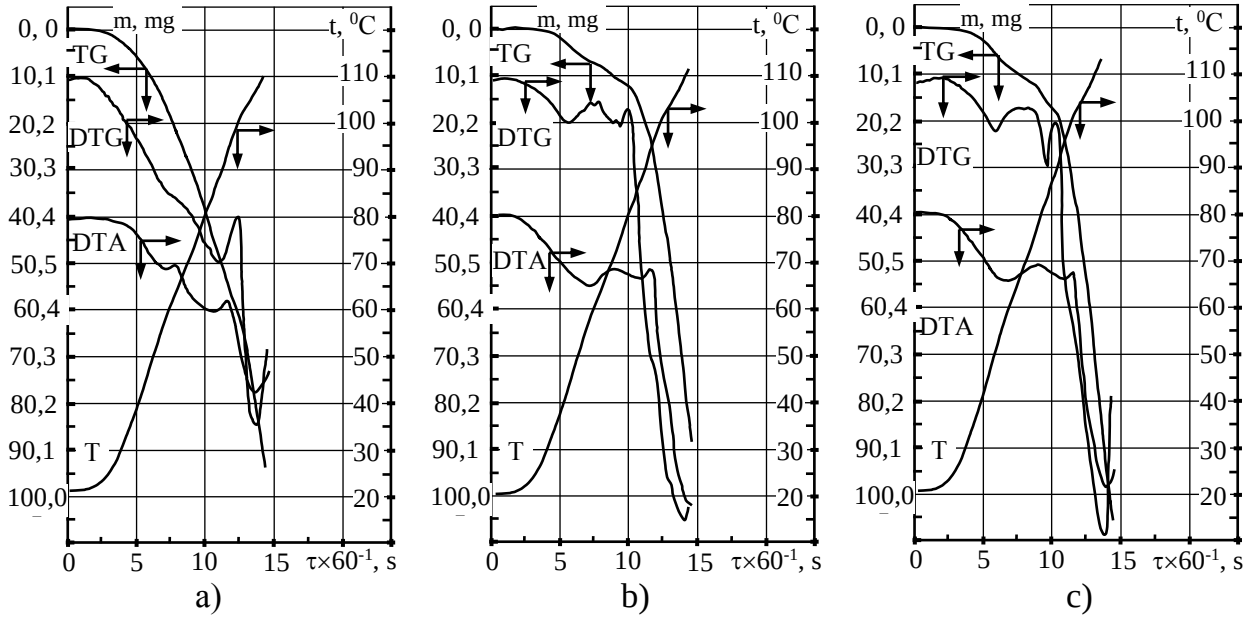


Figure 4.32. The dependence of mass loss (TG), mass loss rate (DTG), thermal effects (DTA) under non-isothermal conditions on the thermal processing duration and temperature (T) with sodium citrate concentrations: a – 1%, b – 2%, c – 3%

Each stage characterizes the relevant process, which takes place in the snack pastes model mixture under thermal effect. The first stage (the temperature is 55±1^{0}C) characterizes the beginning of thermal processing, the second stage (the temperature is 82±2^{0}C) characterizes the ending of thermal processing, the third stage (the temperature is 110±3^{0}C) characterizes the breaking of the structure because of considerable loss of water due to its intensive vaporization.

Table 4.7 shows the maximal temperature values (peaks), which characterize the stages of thermal decomposition of the snack pastes' system samples.

The comparative analysis of thermo-analytical curves (TG, DTG, DTA) of the samples with different sodium citrate contents has shown that the rate of the process of decomposition of the snack pastes' protein base with 1±0.1% sodium citrate concentration is much higher at the first and second stages (the beginning and ending of thermal processing) than with 2±0.1% and 3±0.1% sodium citrate concentration [65].

Table 4.7 – The characteristics of the snack pastes' protein base decomposition

Sodium citrate content, %	Positions of maximums DTG, ^{0}C		
	1 stage	2 stage	3 stage
1.0±0.1	65±1	88±2	105±3
2.0±0.1	58±1	85±2	108±3
3.0±0.1	61±1	94±2	110±3

At all stages of the experimental samples' decomposition there is mass loss due to water vaporization. The greatest mass losses are observed for the sample containing 1.0±0.1 of sodium citrate at the first and second stage. They attain 11.0±0.5% (19.8 mg). The mass losses for the samples containing 2.0±0.1 and 3.0±0.1% of sodium citrate are much lower. They are 2.1±0.5% (3.6 mg) and 2.6±0.5% (4.7 mg) respectively at the first stage, and 3.2±0.5% (5.15 mg) and 4.4±0.5% (8 mg) respectively at the second stage. This means that the snack pastes' model sample with 2.0±0.1% sodium citrate concentration is the most thermally stable.

During heating in the temperature interval of 30…58^{0}C (range I) the intensity of water release from the snack pastes' protein base with 1.0±0.1, 2.0±0.1, 3.0±0.1% sodium citrate concentrations are 6.2±0.4; 2.6±0.2; 2.4±0.2% respectively. This may be non-bound water, which is present in the system's voids.

Within the temperature interval of 50…75^{0}C (range II) the intensity of water release changes and is 8.8±0.5%; 3.5±0.2%; 2.2±0.2% respectively. This may be mechanically bound water, which is present in the milk clot's pockets, which

forms due to casein coagulation and formation of binding bridges between protein stromas from fat globules.

Within the temperature interval of 75…90^{0}C (range III) we observe a significant endothermal peak, which reflects thermal processes taking place in the paste during thermal processing and characterizing the increase of protein's hydration ability caused by temperature, and partial release of water weakly bound to protein. The intensity of water release is 7.2±0.4, 3.2±0.2, 2.2±0.2% respectively.

During heating the snack pastes' protein base at over 90^{0}C within the interval of 105…110^{0}C (range IV) we observe on DTA and DTG curves the marked endothermal peak, which reflects the thermal processes characterizing release of water with different forms of bonds due to the breaking of the protein system. It is obvious that in these temperature intervals there is release of water, which is bound by the adsorption centers of the colloidal system. The intensity of water release is 18.2±0.5, 26.9±0.5, 33.0±0.5% respectively.

There is a certain slowing down of water release between the two first endopeaks (Table 4.7) because of its binding by protein due to the temperature effect. The energy supplied to the samples is spent for destruction processes in the snack pastes' model system mixture. This is confirmed by three endothermal peaks of heat consumption in the indicated temperature intervals on the DTG curve. Taking into consideration the mass loss values at relevant temperature T the pastes dehydration process was quantitatively evaluated by calculating activation energy E (Figure 4.34). The graphs of the dependence of mass losses on temperature lnm–2lnT=*f*(1000/T) (Figure 4.33) in semi-algorithmic coordinates were built to calculate the activation energy and process the experimental data of thermo-analytical curves (TG, DTG, DTA of the samples with different sodium citrate contents.

In the graphs the breaking points coincide with the temperatures of the first and second endopeaks (the beginning and the ending of thermal processing) of DTG curve of different samples. The graphical data let calculate the temperature intervals characteristic of a certain activation energy. Slope ratios were found to calculate it from the graphical dependence of lnm–2lnT on 1000/T, which has a distinct rectilinear character.

The obtained thermo-graphic data confirm that the increase of sodium nitrate concentration in the snack pastes' model system raises the binding energy of water molecules with protein (Figure 4.34). The sample of model system mixture with

2.0±0.1% sodium citrate concentration has greater activation energy compared o other samples, which indicates its greater thermal stability [65, 67].

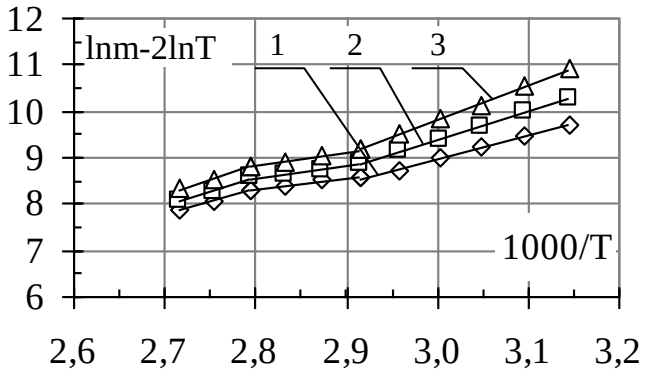


Figure 4.33. The logarithmic dependence of mass losses on the temperature of the pastes' protein base with different sodium citrate contents: 1 – 1.0%, 2 – 2.0%, 3 – 3.0%

The calculated values of possible thermal processing activation energy characterizes the value of binding water of the snack pastes' protein base with different sodium citrate contents: 1.0±0.1%, 2.0±0.1%, 3.0±0.1%, which under non-isothermal conditions of the research are 24.6±1; 33.2±1; 31.5±1 kJ/mole respectively.

The obtained results correlate with the values of the thermal effects for the temperature interval of the process and correspond to the researches of molecular mobility of water using the nuclear magnetic resonance pulse spectrometer [68…72] and to X-ray tests (Figure 4.13) of the structure orderliness of the snack pastes' protein base [41, 42].

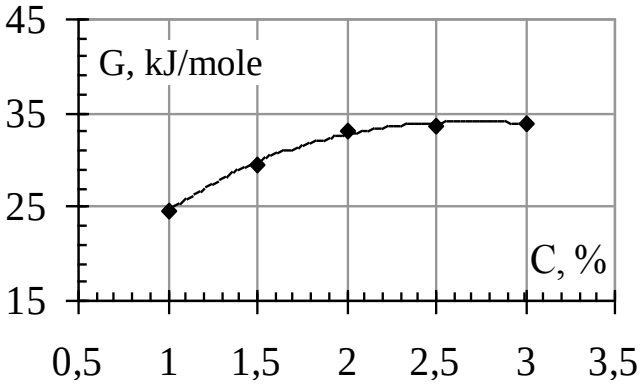


Figure 4.34. Dependence of activation energy on sodium citrate concentration

The endopeak maximums on DTA and DTG curves coincide. This means that at these temperatures there is a reaction, which causes not chemical or physical transformation of protein, but breaking the physical-mechanical and physical-chemical bonds of water with protein base.

To define the dynamics of loss of water, which has different forms of binding with protein [65] during the thermal processing in the model system of snack pastes with different agar contents, the evaluation of the mass of kinetically unequival molecules of water was performed using the experimental curves by thermogravimetry (DTG) and differential thermal analysis (DTA) methods under non-isothermal (Figure 4.35, 4.36) and isothermal (Figure 4.37, 4.38)conditions.

The derivatograph of the snack pastes' model system (Figure 4.35) heps define the temperatures of different degrees of dehydration, destructionof prorein substances and temperature intervals of stability of intermediate compound confirmed by the endothermal effect peaks, which are accompanied by moisture vaporization and possible release of gas fractions.

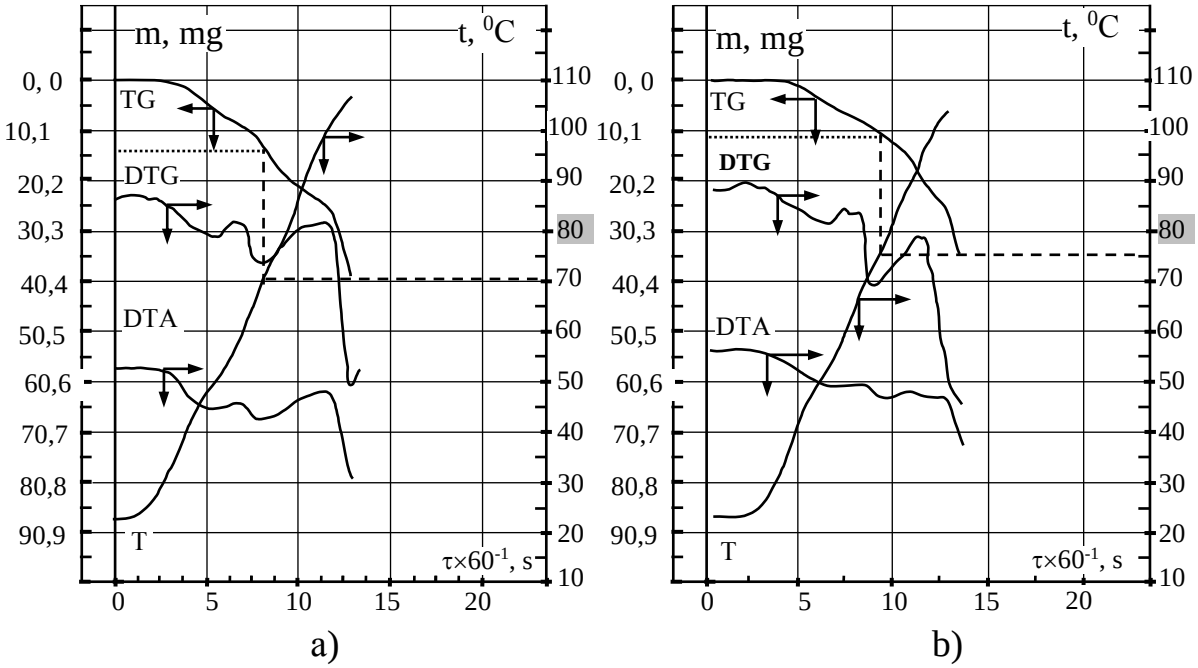


Figure 4.35. The dependence of mass loss (TG), mass loss rate (DTG), thermal effects (DTA) under non-isothermal conditions on the duration of the thermal processing of model system with 40% content of fat-free lactic acid curd, 25% content of vegetable oil, and agar contents : a – 0.0%, b – 1.1%

During heating within 35…55^{0}C interval (range I – the beginning of protein's polymorphic transformations) the endothermal peak appears in all samples, which reflects thermal processes going on in the pastes' model system during intensive water release. Owing to thermal effect water losses of the shack pastes' model system without agar and with 1.1±0.1; 1.3±0.1; 1.5±0.1% concentrations of agar are 11.0±0.5; 5.8±0.3; 4.8±0.2; 3.2±0.2% respectively. This may be unbound or mechanically bound water present in the systems voids.

In 55…75^{0}C temperature interval (range II – the main range of thermal processing for the paste's model system) the endothermal peak in the samples

without agar appears at 70±2 ^{0}C, and in the samples with 1.1±0.1% agar concentration it appears at 75±2 ^{0}C. The peak reflects the thermal processes going on in the snack pastes' model system during the thermal processing. The intensity values of water release change in respect to agar concentrations. They are 7.6±0.5, 5.9±0.5, 4.4±0.2, 3.7±0.2%.

In 56…86^{0}C temperature interval (range II – the main range of thermal processing for the paste's model system with 1.3…15% agar comcentration) the endothermal peak appears on the DTA curve in the samples with 1.3±0.1% agar concentration at 80±2^{0}C, and in the samples with 1.5±0.1% agar concentration at 85±2^{0}C, which reflects the thermal processes going on in the snack pastes' model system during the completion of the thermal processing and characterize the increase of protein's hydration ability under temperature effect and partial release of adsorptionally bound water, which is weakly bound with protein. The intensity values of water losses respective to agar concentrations are 10.2±0.5; 5.4±0,2; 4.3±0.1; 3.4±0.1%.

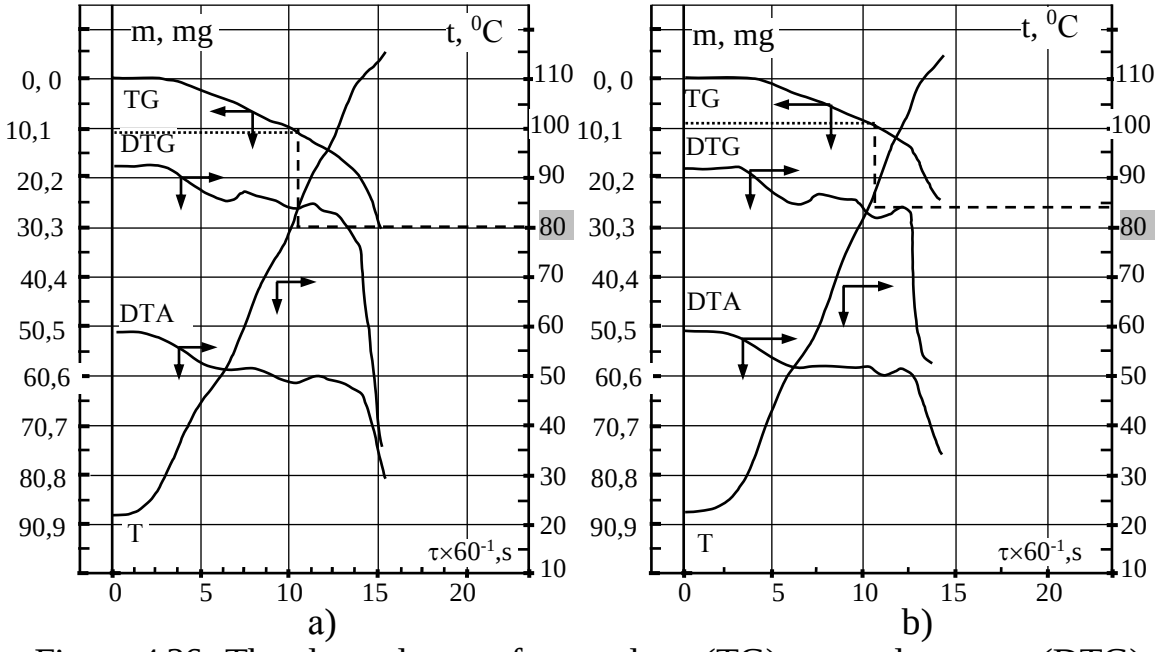


Figure 4.36. The dependence of mass loss (TG), mass loss rate (DTG), thermal effects (DTA) under non-isothermal conditions on the duration of the thermal processing of model system with 40% content of fat-free lactic acid curd, 25% content of vegetable oil, and agar contents : a – 1.3%, b – 1.5%

In 95…115^{0}C temperature interval (range III – destructive changes in the pastes' model system with any agar concentration) the sharp endothermal peak appears in all samples. It reflects the thermal processes going on in the snack pastes' model system during the breaking of the protein' s structure with the release of gas-like fractions.

With the purpose of obtaining the data concerning water release mechanism the TG curve was used to calculate the degree of changing mass α (Figure 4.37) and the dependence $|-lg\alpha|$ on the value of reverse temperature 1000/K (Figure 4.38) was built. It was done for the temperature interval of 55…95 ^{0}C, because this is the interval, within which there are the most intensive processes of the snack pastes model system's hydration demonstrated by the endoeffects on the derivatogram graphs (Figure 4.35, 4.36).

The rate of mass change, which corresponds to the process of dehydration, was used to determine the dependence of mass change on temperature. To do this a sample's mass change Δm_1, which corresponds to the amount of water released at this temperature, was found for constant temperature intervals of 5^{0}C along the TG curve.

The degree of the change of mass α (Figure 4.37) was calculated using the DTG curve as the ratio of Δm_1 to the total amount of water in the model system released at the end of the process of dehydration. The total mass loss at 95 ^{0}C in snack pastes without agar (sample 1) is 15.5%, in snack pastes with 1.1% agar (sample 2) is 14.85%, %, in snack pastes with 1.3% agar (sample 3) is 12.5%, and in snack pastes with 1.5% agar (sample 4) is 9.92%.

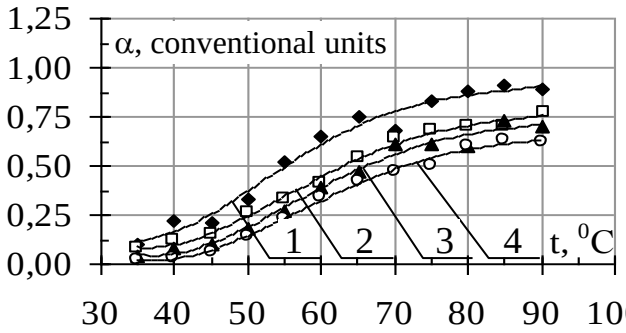


Figure 4.37. The dependence of the degree of mass change in the model snack paste with agar contents: 1 – 0.0%, 2 – 1.1%, 3 – 1.3%, 4 – 1.5% on temperature

The obtained TG curves in α-t coordinates (Figure 4.37) are S-shaped, which characterizes the interaction forms between water and solids in snack pastes with different agar concentrations, and, as a result of these interactions, the differences in the rates of water release during heat processing. Thus, the curves of the dependence of the of the model snack paste' mass change on temperature let investigate the kinetics of unequal forms of moisture binding and reflect different rates of dehydration of finished products.

During the first stage at 310…323^0 K (Figure 4.38 stetch *AB*) the release of "free" or mechanically bound (capillary) moisture, which has low binding energy with the product, takes place. First, water, which forms the structural grid of water molecules bound with each other by hydrogen bonds, releases. Here the capillary water desorption is characterized by lower values of activation energy compared to water released during the second stage of the process.

At the second stage (stretch *BC*) during heating at 323…358^0 K a part of osmosis and immobilization bound water retained in closed areas of protein micelles is freed due to the unfolding of their polypeptide chains, because of breaking micellar and hydrophobic interactions of proteins with water.

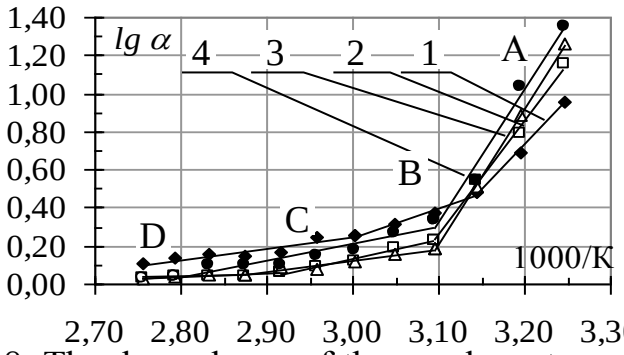


Figure 4.38. The dependence of the snack paste model system's mass change degree logarithm on temperature with agar contents: 1 – 0.0%, 2 – 1.1%, 3 – 1.3%, 4 – 1.5%

In the temperature interval of 358…363^0 K during the third stage (stretch *BD*) the release of insignificant pat of weakly bound adsorptional water of polymolecular layers inside the model emulsion's particles begins. The water released forms next several layers of molecules more strongly bound with snack paste model system's protein.

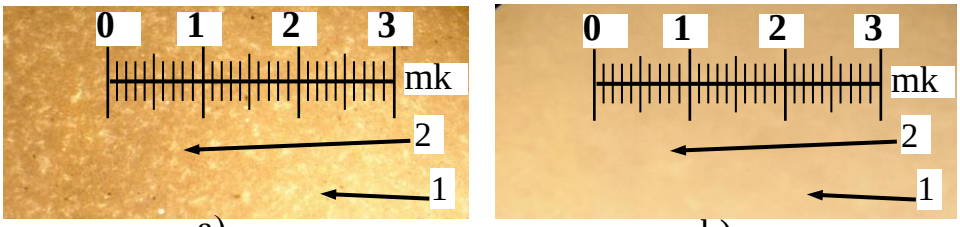
At 363…388^0 K there is probable destruction of protein substances of the snack pastes' model system, which is accompanied by the ending of intensive mass loss. The sharp peak of endothermal effect at 388^0 K, probably, characterizes the process of the release of the molecules of strongly bound adsorptional moisture and chemically bound moisture with the release of gas-like fractions and breaking of the protein's structure.

Thus, during heating under non-isothermal conditions the temperature interval of the weakly bound moisture release is about the same. In the samples without agar it is 35…45^{0}C, in other samples it is within 35…50^{0}C. The temperature intervals of the release of osmosis-bound moisture rise with the increase of agar contents: 0.0; 1.1±0.1; 1.3±0.1; 1.5±0,1% to 45…68^{0}C, 50…72^{0}C, 50…80^{0}C,

50…85^{0}C respectively. The temperature intervals characterizing the release of adsorption-bound moisture decrease with the increase of agar contents. They are 68…90^{0}C, 72…90^{0}C, 80…90^{0}C, 85…90^{0}C respectively. The sample's mass only decrease sharply at over 95^0 C, which may be explained by the complexity of the macromolecular structure of the snack pastes' model system. It probably happens due to adding agar to the recipe, which provides for a higher degree of macromolecular binding (Figure 4.41) and slows down dehydration [64, 65]. The complete decomposition of the snack pastes' model system with the destruction of protein and loss of all moisture contained in the system takes place at temperatures over 115±3^{0}C .

The microphotograph of the snack pastes' model system during heat processing (Figure 4.39 a) confirms that after adding agar the structural grid forms, which almost cannot be observed visually the next after (2±1)×60 s of heat processing (Figure 3.41 b), probably, due to binding with protein macromolecules. Arrows 1, 2 in the microphotographs point to the elements of the structural grid formed by agar.

Thus, the analysis of the obtained data allowed to identify the temperature zones characterizing three stages of moisture vaporization (Figure 4.38) with different energy, which forms during the snack pastes heat processing due to agar concentration.



a) b)

Figure 4.39. The microphotograph of the snack pastes' model system during heat processing: a – after adding agar, b – after (2±1)×60 s

The derivatogram (Figure 4.35, 4.36) analysis established that the increase of agar concentration from 1.0±01% to 1.5±01% raises the processing temperature from 75±2 ^{0}C to 95±2^{0}C, which conforms to the previous research (Figure 4.28). It lowers moisture loss by 1.5…3% during processing due to its retention in the protein grid (Figure 4.39).

To determine the rational duration of heat processing of the samples with different agar content thermogravimetric tests were performed under isothermal conditions (Figure 4.40, 4.41), accepting the maximal processing temperature of 90±2 ^{0}C owing to the previous research outcomes (Figure 4.37, 4.38).

The research have shown that under isothermal conditions the process of moisture loss due to water vaporization during thermal processing in all snack paste model system samples goes on enothermally in two stages.

Two endoeffects have been recorded on each DTG curve in the temperature intervals respective of agar contents in the pastes' recipes: 0.0% –45 and 72^{0}C; 1.1% – 50 and 75^{0}C; 1.3% – 50 and 78 ^{0}C; 1.5% – 50 and 80 ^{0}C [63, 66].

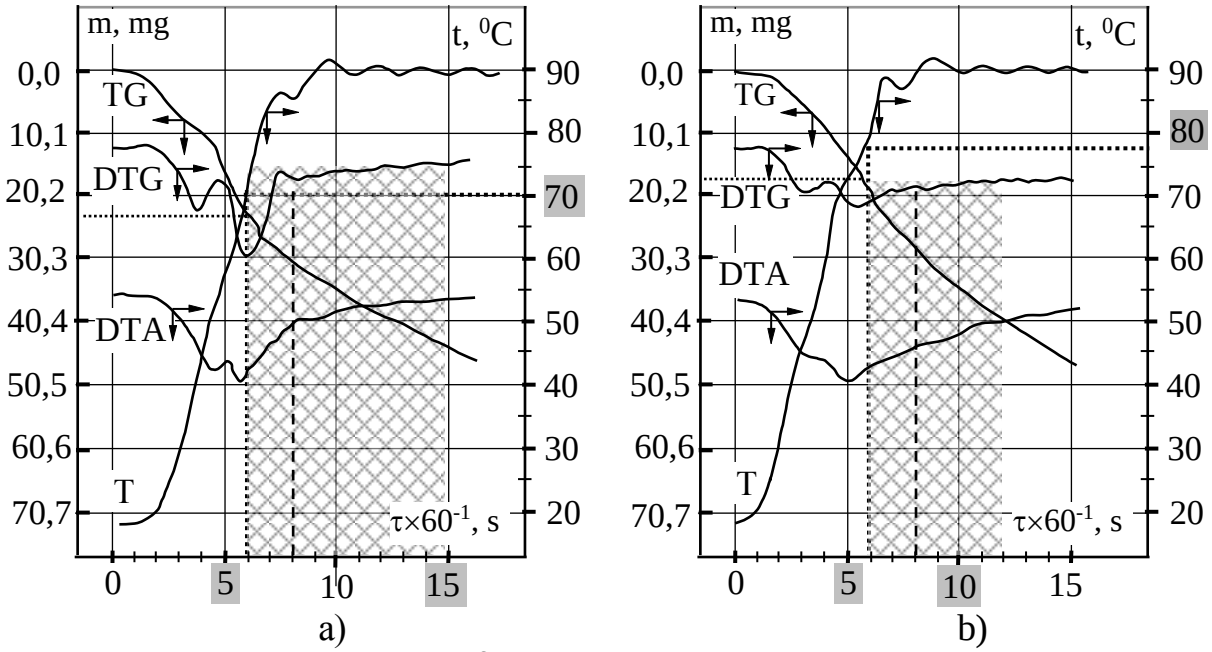


Figure 4.40. The dependence of mass loss (TG), mass loss rate (DTG), thermal effects (DTA) under isothermal conditions on the duration of thermal processing of model system with 40% fat-free lactic acid curd content, 25% vegetable oil content, agar contents: a – 0.0%, b – 1.1%

Since the snack paste model system is a colloidal capillary-porous system as to its moisture binding forms, its moisture is bound with protein due to physical-mechanical and physical-chemical bonds [64, 65]. Probably, its moisture retaining capability mostly depends on the mechanically and adsorption bound water content [73, 74].

The derivatogram (Figure 4.40, 4.41) analysis established that the main thermal processes going on in the snack pate model system during heat processing characterize the hydration ability of protein affected by temperature, sodium citrate and agar, as well as partial release of water weakly bound with protein, which go on during (8±2)×60 s. Moisture losses during this period of time depend on agar concentrations: 0.0%; 1.1±0.1%; 1.3±0.1%; 1.5±0.1%. They are 30.3±1%; 18.5±0.5%; 16.2±0.5%; 15.1±0.5% respectively. During further heating of snack

pastes for (2±0.5)×60 s there is leveling of temperature in the product and moisture loss increase by approximately 10…20%.

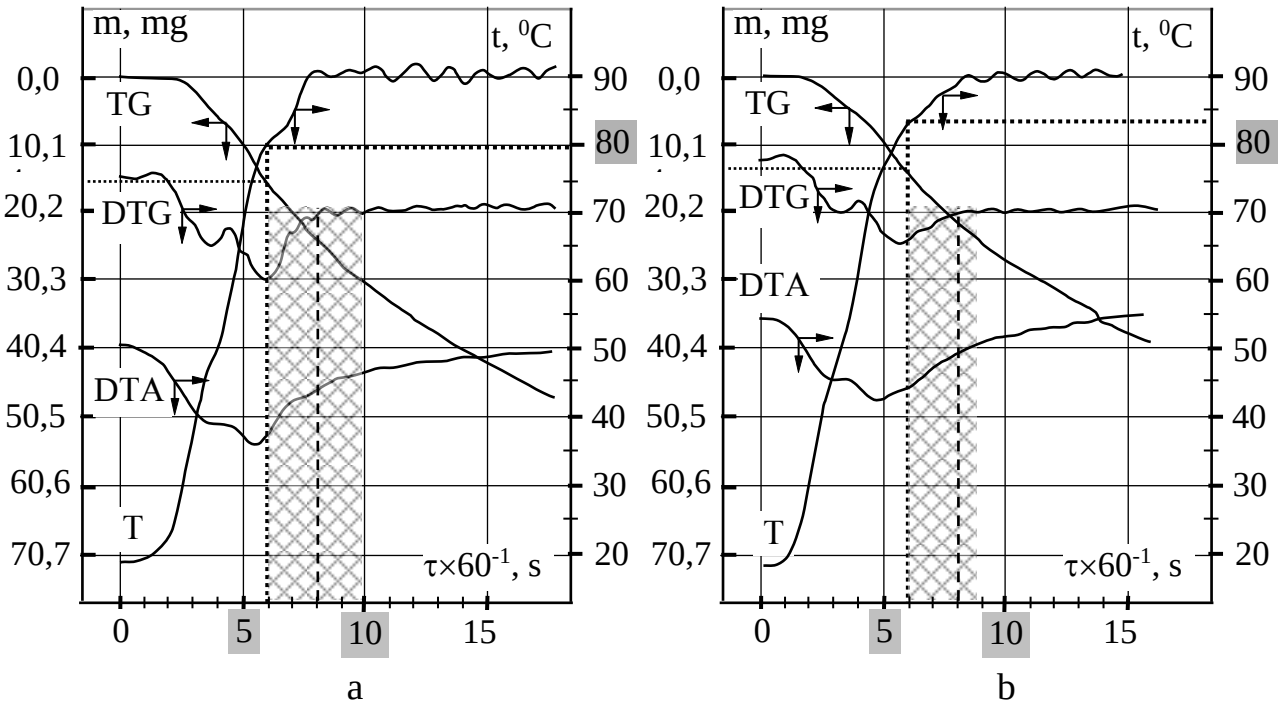


Figure 4.41. The dependence of mass loss (TG), mass loss rate (DTG), thermal effects (DTA) under isothermal conditions on the duration of thermal processing of model system with 40% fat-free lactic acid curd content, 25% vegetable oil content, agar contents: a – 1.3%, b – 1.5%

Thus, the thermogravimetric tests of the snack paste samples with different agar content make it possible to estimate the amount of free and bound water, energy consumption by dehydration, as well as determine the rational duration of the heat processing of pastes as (8±2)×60 s.

4.3.2 Investigating the Forms of Moisture Retention

The quantitative content of moisture in the product, as well as the ratio of free and bound water play important roles in the structure formation of the finished product and stabilization of the snack pastes' system [27].

The research to determine the changes of the time of spin-spin relaxation of water dipole (Figure 4.42) depending on the components' concentration in the snack pastes' model system at all stages of the technological process was performed by the spin echo method [68, 69, 71, 73, 74].

It has been established that the dependences of the time of spin-spin relaxation of water dipole (T_2) on the recipe components have the appearance of smooth curves (Figure 4.42), which characterize the trend towards the decrease of T_2 value

with the increase of sodium of citrate content. Each curve characterizes the effect of a certain recipe component. Thus, owing to adding vegetable oil in the recipe mixture prepared for thermal processing, T_2 decreases by $3 \cdot 10^{-2}$ s.

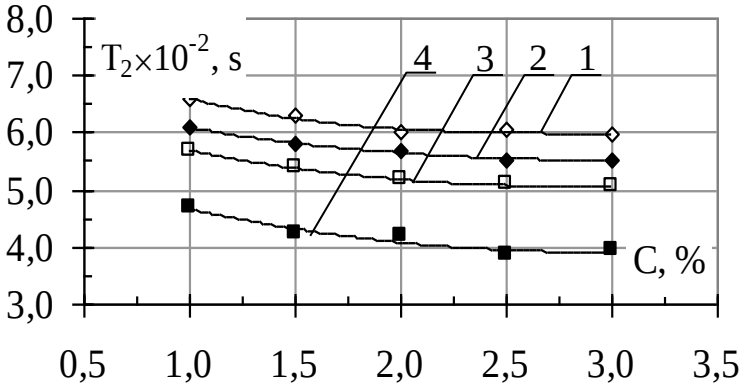


Figure 4.42. Dependence of the time of spin-spin relaxation of water dipole in the model system of snack pastes on sodium citrate concentration before thermal processing: 1 –without oil, 2 –with oil; after thermal processing: 3 –without agar, 4 – with agar

After the snack pastes' thermal processing T_2 decreases by further $6 \cdot 10^{-2}$ s, and adding agar to the recipe mixture decreases the time of spin-spin relaxation by $12 \cdot 10^{-2}$ s. This is explained by the effect of technological factors on the increase of moisture retaining capability of protein, which causes the decrease of the amount of "free" water in the snack paste (Figure 4.43).

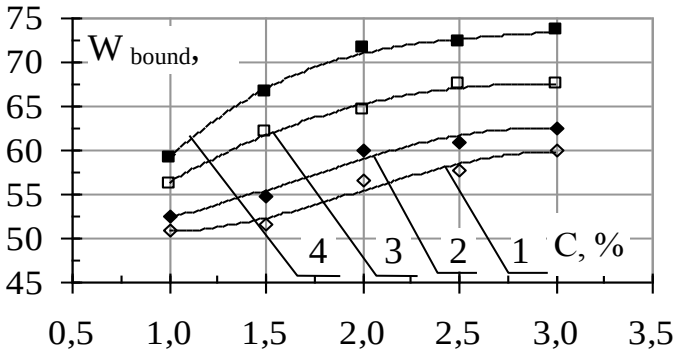


Figure 4.43. The dependence of mass part of bound water in the model system of snack pastes on sodium citrate concentration before thermal processing: 1– without vegetable oil, 2 – with vegetable oil; after thermal processing with vegetable oil: 3 –without agar, 4– with agar

The graphs show that adding vegetable oil, agar to the recipe, as well as thermal processing decrease the time of spin-spin relaxation of water dipole in the snack paste. The increase of sodium citrate concentrations from 1.1% to 2.0% decreases T_2 by $5 \cdot 10^{-2}$ s, and form 2.0% to 3.0% - only by $1 \cdot 10^{-2}$ s.

After doing the calculations of the obtained data concerning the kinetics of spin-spin relaxation of water dipole in the snack paste we investigated the effect of the basic components on the kinetics of binding water by the snack pastes' protein at different stages of their production (Figure 4.43) depending on melting salt concentration.

The tendency towards the increase of bound water when adding vegetable oil, which emulsifies into the model paste mixture, and a significant increase of bound water after adding agar and thermal processing has been established. Moreover, the increase of sodium citrate concentration in the snack paste also causes the increase in the amount of water bound by protein. The character of the curve (Figure 4.43) shows that the increase of sodium citrate concentration in the finished product by more than 2.0% does not affect the amount of "bound" water (Table 4.8).

The analysis of the graphs (Figure 4.43) shows that the protein of the snack paste model system with 2.0±0.2% sodium citrate concentration before the technological processing is capable of binding up to 56±2% of moisture. After the emulsification of sunflower oil the amount of bound moisture increases by further 3.0%, and after the thermal processing the snack paste model system's protein is capable of binding up to 65±1% of moisture.

Table 4.8 – The mass part of bound moisture in the snack paste model system at different stages of the technological process

Sodium citrate content, %	Fat-free lactic acid curd content, %	Mass part of moisture bound by protein, %			
		before thermal processing		after thermal processing	
		without oil	with oil	without agar	with agar
0	40	55.15±0.5	55.15±0.6	55.15±0.7	55.15±0.8
1	40	52.63±0.5	54.85±0.5	57.36±0.5	62.55±0.5
2	40	60.06±0.5	62.45±0.5	64.84±0.5	71.73±0.5
3	40	62.31±0.5	64.23±0.5	68.04±0.5	73.54±0.5

After adding agar to the recipe this index increases by 6% and attains 71±1%. In the snack paste model sample with 1±0.1% sodium citrate concentration the amount of bound water is 12% less than in the sample with 2±0.1% sodium citrate concentration and attains 60±2%. In the snack paste model sample with 3±0.1% sodium citrate concentration the amount of bound water is only 2% greater than in the sample with 2±0.1% sodium citrate concentration and attains 73±2%.

Thus, it has been established that during sunflower oil emulsification the mass part of bound water of the protein base of the paste model system with 2±0.1% sodium citrate concentration increases by 4.8±0.1%. The thermal processing at 80 ± 2^0C contributes to increasing the amount of bound water in the snack paste model system by 5.2±0.1%, and adding agar as structure former to the recipe increases the mass part of bound water by further 6.8±0.1%.

4.3.3 Modeling the Process of Thermal Processing

To verify the adequacy of the effective use and effect of main components on the temperature of the thermal processing of snack paste model system with the objective of optimization of their concentrations, determination of optimal limits of the thermal processing temperature on the basis of the experimental data (Figures 4.26…4.28, 4.35, 4.36, 4.38, 4.40, 4.41) we have modeled the process of the thermal processing of snack paste model system depending on the concentrations of the main ingredients. Here, we have taken into consideration that the changing parameters of the process are the temperature and processing duration.

We used the correlation-regressive method applied to model pairs: fat-free lactic acid curd – vegetable oil (Figure 4.44), fat-free lactic acid curd – agar (Figure 4.45) to determine the rational concentrations of the components of the snack paste model system. We based our research not only on the terminalization coefficients, but also on the adequacy of physical-chemical model of the process of thermal processing, the similarities of the forms of biding of agents [75…78].

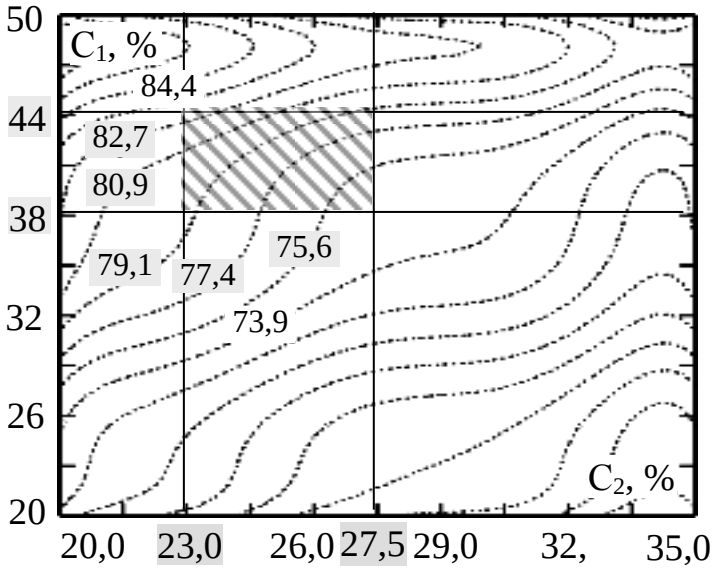


Figure 4.44. The dependence of the lines of equal values of thermal processing of the pair model of the paste on the main components' concentrations of: C_1 – fat-free lactic acid curd; C_2 – vegetable oil

The modeling of the kinetics of the thermal processing isotherms was carried out to determine the common optimal areas of the thermal processing temperatures in the normalized space on the basis of the experimental data. The optimal limits of concentrations of the ingredients of the snack paste model system were determined. They are: 38…44% of fat-free lactic acid curd, 23.0…27.5% of vegetable oil, 1.22…1.34% of agar.

The obtained lines of equal values of temperature as function of the main components' concentrations $t_{пл}=f(C_1;C_2)$ within the model pair (Figure 4.44) with 38…44% concentration of lactic acid curd and 23.0…27.5% of purified deodorized oil proved that the optimal temperature of thermal processing is within 78±3 ^{0}C.

The obtained dependences of the lines of equal values of temperature $t_{пл}=f(C_1;C_3)$ as function of the main components' concentrations: 38…44% of lactic acid curd, 1.22…1.34% of agar within the model pair (Figure 4.45) showed that the optimal temperature of thermal processing of this snack paste model system is within 80±3 ^{0}C.

According to Fischer criterion no less than 94% of statistical dependence of the thermal processing temperature on the main components of the snack paste model system (Figure 4.44…4.46) is described by the obtained regressive curves [75, 77].

After defining the rational limits of parameters we built a three-dimensional model (Figure 4.46) of the dependence of the thermal processing temperature on the concentrations of the two parameters ($C_3^2=3$ variants).

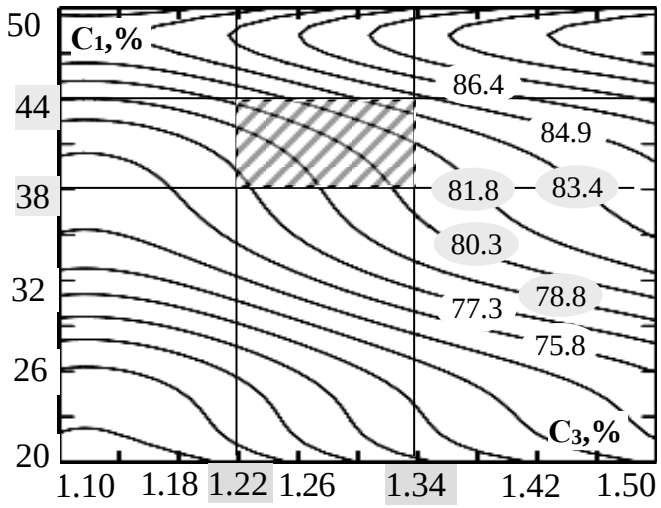


Figure 4.45. The dependence of the lines of equal values of thermal processing of the pair model of the paste on the main components' concentrations of: C_1 – fat-free lactic acid curd; C_3 – agar

By the normalization of the main ingredients' concentrations in relation to the rational limits we obtained a graphic image of the lines of equal values of thermal processing of the snack pastes' model system for different pairs of dependences (Figure 4.46).

The mathematical modeling helped define the optimal values of the main components in the basic recipe of the snack pastes' model system: lactic acid curd - 40±2%, purified vegetable oil - 25±1%, agar – 1.3±0.1% and the thermal processing temperature within 80±2^{0}C, which conforms to the previous experimental research.

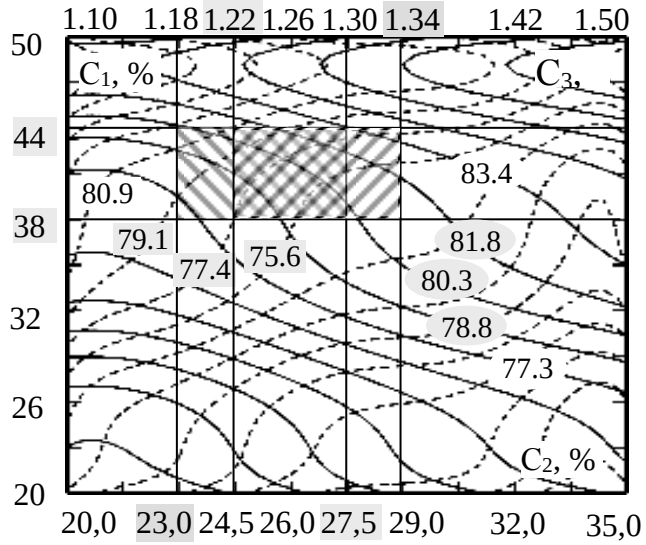


Figure 4.46. The dependence of the temperature of the thermal processing of the model system on the optimal concentration values of the ingredients: C_1 – lactic acid curd; C_2 – vegetable oil; C_3 – agar

Our snack pastes' model system does not contain traditional protein raw material characteristic of such products, i.e. rennet curds. Moreover, purified deodorized vegetable oil is used as a fat component. So, the production technology of snack pastes needs creating a certain set of conditions for their thermal processing and production of the finished product of high consumer satisfaction [27, 76, 79, 80].

4.4 Researching the Structural-mechanical Characteristics of the Snack Pastes' Model System

The structural-mechanical properties of real bodies, disperse and high-molecular systems are directly linked to molecular interactions in these bodies, their structural specifics and thermal movement of their structural elements – micelles, submicelles and macromolecules, the interactions of these elements with each other and with molecules of disperse environment. So, the structural-

mechanical properties characterize the emergence of structures of different kinds in the system. The elastic-plastic-viscous properties on the one hand, and the properties of strength of the model system on the other hand determine the character of their deformational processes and processes of destruction.

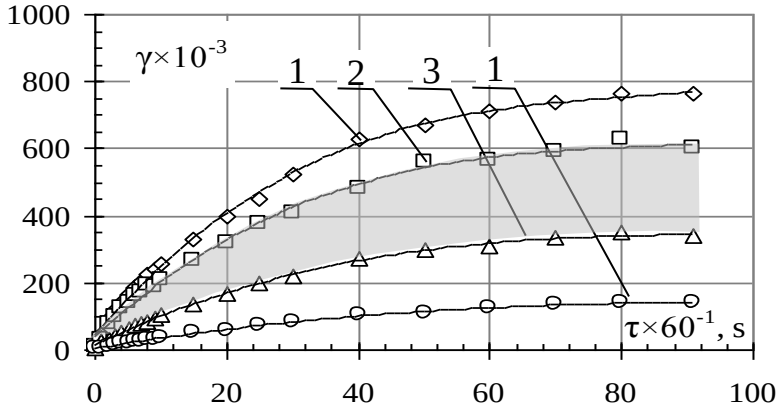


Figure 4.47. The kinetics of creep curves of pastes' model system with different concentrations of fat-free lactic acid curd: 1– 25%, 2 – 30%, 3 – 40%, 4 – 50%

The structural-mechanical properties (relative: deformation, elasticity, plasticity, resilience) were determined with the help of D.M. Tolstoy's elasto-plastometer [81-84] by investigating the shear deformation of the snack pastes' model system, placed between the plates. The experimental data were presented in the form of creep curves (Figure 4.47, 4.48, 4.49) building the dependence of relative deformation on strain duration $\gamma=f(\tau)$ [156, 157].

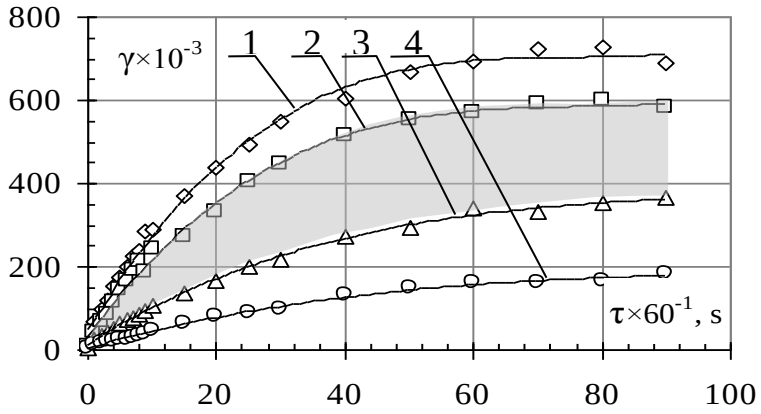


Figure 4.48. The kinetics of the creep curves of snack pastes' model system with different contents of vegetable oil: 1 – 15%, 2 – 20% , 3 – 25% , 4 – 30%

The development of the new technology of snack pastes calls for extensive research of structural-mechanical properties of raw materials, semi-finished and finished products necessary for the proper conduct of technological processes, their mechanization and automation. These properties affect all the various

processes: thermal, mechanical, diffusion, which are responsible for a finished product's flavor and digestibility [84…86].

Table 4.9, 4.10. 4.11 shows the results of the research of the main recipe components' effects on the deformation kinetics and the calculations of rheological characteristics of the snack pastes' model system.

Table 4.9 –The structural-mechanical characteristics of the snack pastes' model system with 25% vegetable oil and 1.3% agar content depending on the lactic acid curd content

Symbols	Indices	Lactic acid curd content , %			
		25	30	40	50
$\gamma_{зв.}$	Reversible deformation,10^{-3}	420.80	338.20	187.30	56.20
$\gamma_{нез.}$	Irreversible deformation, 10^{-3}	359.20	297.80	181.70	99.80
$\gamma_{заг.}$	Total deformation, 10^{-3}	780.00	636.00	369.00	156.00
P	Shear strain, Pa	32.70	32.70	32.70	32.70
I	Compliance, Pa^{-1}	$2.3\ 10^{-2}$	$1.94\ 10^{-2}$	$1.13\ 10^{-2}$	$4.77\ 10^{-3}$
$G_{пр.}$	Conditionally instantaneous coefficient of elasticity, Pa	2289,0	3433.5	5722.5	8692.4
$G_{ел.}$	High-elasticity coefficient, Pa	80,44	99.49	180.08	623.59
η	Viscosity, Pa×s	$4.88\ 10^5$	$5.84\ 10^5$	$9.57\ 10^5$	$1.75\ 10^6$
K	Ratio $\gamma_{зв./}\gamma_{заг.}$	0.54	0.53	0.51	0.36
$Пр$	Relative elasticity, %:	1.83	1.50	1.55	2.41
$Пл$	Relative plasticity, %:	46.05	46.82	49.24	63.97
$Ел$	Relative spring, %:	52.12	51.68	49.21	33.61
Θ	Relaxation period, s	6280.60	6039.29	5481.95	3010.71

The analysis of the snack paste model system's creep (Figure 4.47, 4.48, 4.49) has shown that after shear strain 32.7±1.5 Pa during (50…60)×60 s all researched samples with different recipe components content had the same total deformation. This means that further strain causes the snack paste model system's creep. This proves that the shear strain on the upper plate was chosen correctly [27, 81, 82, 84, 87, 88].

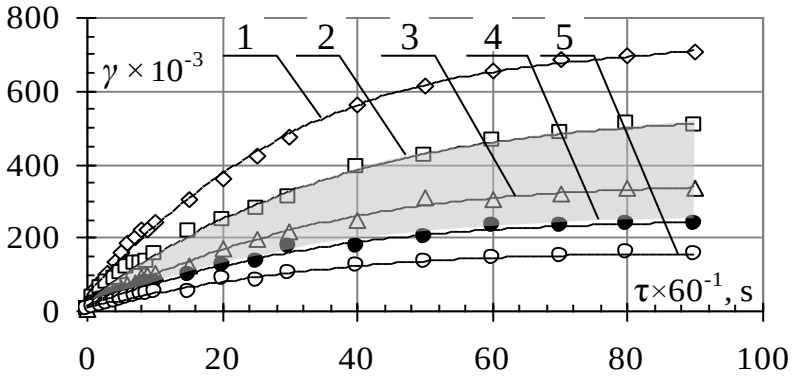


Figure 4.49. Kinetics of the creep curves of snack pastes' model system with different contents of agar: 1 – 1.1%, 2 – 1.2% , 3 – 1.3% , 4 – 1.4%, 5 – 1.5%

The creep curves of the snack paste model system show that the most fluid are the following samples: the sample with 25±2% lactic acid curd content with total deformation $780.0 \cdot 10^{-3}$; the sample with 15±5% purified deodorized vegetable oil content with total deformation $740.0 \cdot 10^{-3,}$, and the sample with 1.1±0.2% agar content with total deformation $721.0 \cdot 10^{-3}$.

Table 4.10 – The structural-mechanical characteristics of the snack pastes' model system with 40% fat-free lactic acid curd, 1.3% agar on depending on the vegetable oil content

Symbols	Attributes	Vegetable oil content, %			
		15	20	25	30
$\gamma_{зв.}$	Reversible deformation,10^{-3}	451.30	370.70	184.39	60.90
$\gamma_{нез.}$	Irreversible deformation, 10^{-3}	288.70	249.30	187.04	134.10
$\gamma_{заг.}$	Total deformation, 10^{-3}	740.00	620.00	371.43	195.00
P	Shear strain, Pa	32.70	32.70	32.70	32.70
I	Compliance, Pa^{-1}	$2.26\ 10^{-2}$	$1.90 \cdot 10^{-2}$	$1.14 \cdot 10^{-2}$	$5.96 \cdot 10^{-3}$
$G_{пр.}$	Conditionally instantaneous coefficient of elasticity, Pa	4291.88	4905.00	5722.50	7785.71
$G_{ел.}$	High-elasticity coefficient, Pa	73.70	89.83	183.02	576.72
η	Viscosity, Pa×s	$6.07 \cdot 10^{5}$	$7.03 \cdot 10^{5}$	$9.35 \cdot 10^{5}$	$1.33 \cdot 10^{6}$
K	Ratio $\gamma_{зв./}\ \gamma_{заг.}$	0.61	0.60	0.50	0.31
$Пр$	Relative elasticity, %:	1.03	1.08	1.54	2.15
$Пл$	Relative plasticity, %:	39.01	40.21	50.36	68.77
$Ел$	Relative spring, %:	59.96	58.72	48.10	29.08
Θ	Relaxation period, s	8383.28	7972.04	5271.75	2485.71

The most resistant to shear strain are the samples with the following contents: 50±2% of lactic acid curd with total deformation $158.0 \cdot 10^{-3}$, 30±5% of vegetable oil with total deformation $188.0 \cdot 10^{-3}$, 1,5±2% of agar with total deformation $153.0 \cdot 10^{-3}$ (Table 4.9, 4.10, 4.11), which conforms to the organoleptic indices of the product [89…91].

It has been established that 40±2% concentration range of lactic acid curd, 25±2% concentration range of oil, 1.3±0.1% concentration range of agar (Figure 4.47, 4.48, 4.49) in the snack pastes' model system are rational and make it possible to regulate the consistency of a finished product within the limits necessary for paste products.

The analysis of the tables of the dependence of the coefficients on the recipe components' concentrations shows that the conditionally instantaneous coefficient of elasticity increases: by 17.2±0. 5% within 20 …30% of lactic acid curd concentration range, by 33.2±0.5% within 30…40% concentration range, and by

40.8±0.5% within 40 …50% concentration range; by 12.5±0.2% within 15 …20% of vegetable oil concentration range, by 14.3±0.2% within 20…25% concentration range, and by 44.±1.2% within 25…30% concentration range; by 33.1±1.3% within 1.1 …1.3% of agar concentration range, and by 49.3 ±1.2% within 1.3 …3.5% concentration range. The increase of curd content in the model paste recipe to over 40% causes a sharp increase of the coefficient of elasticity, which makes the structure denser, probably, due to the strengthening of protein's intermolecular action and the transformation of structure from paste-like into slice-like. The increase of vegetable oil content in the paste model system recipe to over 30% causes a sharp increase of the coefficient of elasticity, which makes the structure viscous, probably, due to the strengthening of protein's intermolecular bonds with oil, the increase of its emulsification ability because of the decrease of the amount of free moisture. The increase of agar content in the paste model system recipe to over 1.5±0.1% causes a sharp increase of the coefficient of elasticity, which makes the structure much denser, probably, due to the strengthening of the structure former's spatial grid and the transformation of structure from paste-like into slice-like, and then into hard.

The decrease of curd content in the recipe of paste model system to under 30% causes a significant decrease of the coefficient of elasticity and causes structure fluidity, probably, due to the weakening of milk protein's intermolecular action and the transformation of paste structure into fluid. The decrease of oil content in the recipe of paste model system to under 20±2% also causes the decrease of the coefficient of elasticity and causes structure fluidity, probably, due to the weakening of moisture bonds with protein because of moisture excess. The decrease of agar content in the recipe of paste model system to under 1.2±0.1% causes a significant decrease of the coefficient of elasticity and increase in structure fluidity, probably, due to the weakening of the structure former's spatial grid and the destruction of paste-like structure.

The influence of the recipe components in the snack paste model system on high-elasticity coefficient (Table 4.9, 4.10, 4.11) is insignificant. It grows slowly and only significantly rises when fat-free lactic acid curd concentration is 50±5%, vegetable oil concentration is 30±2%, agar concentration is 1.5±0.1%.

The calculations of plasticity, elasticity and spring (Table 4.9, 4.10, 4.11) confirm that the plastic properties of the paste model system are provided for by: 40±2% fat-free lactic acid curd concentration, 25±2% vegetable oil concentration, 1.3±0. % agar concentration. The tables show that plasticity and spring have the

least difference in this range of components content: lactic acid curd – 4.7±0.8%; vegetable oil - 10±1.2%; agar -12±1.5%.

Table 4.11 – The structural-mechanical characteristics of the snack pastes' model system with 25% vegetable oil and 1.3% agar content depending on agar content

Symbols	Indices	Agar content, %				
		1.0	1.2	1.3	1.4	1.5
$\gamma_{зв.}$	Reversible deformation,10^{-3}	392.30	290.40	205.30	157.20	109.90
$\gamma_{нез.}$	Irreversible deformation, 10^{-3}	328.70	226.60	157.70	80.80	43.10
$\gamma_{заг.}$	Total deformation, 10^{-3}	721.00	517.00	363.00	238.00	153.00
P	Shear strain, Pa	32.70	32.70	32.70	32.70	32.70
I	Compliance, Pa^{-1}	2.2010^{-2}	1.5810^{-2}	1.1110^{-2}	7.2810^{-3}	4.6810^{-3}
$G_{пр.}$	Conditionally instantaneous coefficient of elasticity, Pa	3815.0	4302.6	5722.5	6812.5	11275.8
$G_{ел.}$	High-elasticity coefficient, Pa	85.22	115.63	163.84	214.57	305.61
η	Viscosity, Pa×s	5.3210^{5}	7.6610^{5}	1.5210^{6}	2.1310^{6}	4.0010^{6}
K	Ratio $\gamma_{зв./}\gamma_{заг.}$	0.544	0.56	0.57	0.66	0.72
$Пр$	Relative elasticity, %:	1.19	1.47	1.57	2.02	1.90
$Пл$	Relative plasticity, %:	45.59	43.83	43.44	33.95	28.17
$Ел$	Relative spring, %:	53.22	54.70	54.98	64.03	69.93
Θ	Relaxation period, s	2607.36	6806.25	9548.84	10252.17	13457.14

The increase of lactic acid curd content in the recipe of paste model system to over 45% causes 21.4±1.2% increase of plasticity (Table 4.9), a significant increase of elasticity by 63.4±1.2%, and a significant decrease of spring by 34.6±1.2%. Such decrease of spring and increase of elasticity causes texture crumbling. The increase of vegetable oil content in the recipe of paste model system to over 28% (Table 3.10) causes 20.2±1.0% increase of plasticity, 9.4±0.6% increase of elasticity, and 26.9 ±1.3% decrease of spring. The increase of agar content in the recipe of paste model system to over 1.4% (Table 3.11) causes 35.1±1.5% decrease of plasticity, 21.4±1.2% increase of elasticity, and 25.2±0.5% increase of spring. Such decrease of plasticity, increase of elasticity and spring causes rubber-like texture.

The investigation of strain relaxation (Figure 4.50, 4.51, 4.52) not only makes possible to compare the samples, but also has a great practical importance. Elastic

properties of the structure decrease and plastic properties increase during the relaxation of strains [27, 83, 84, 87].

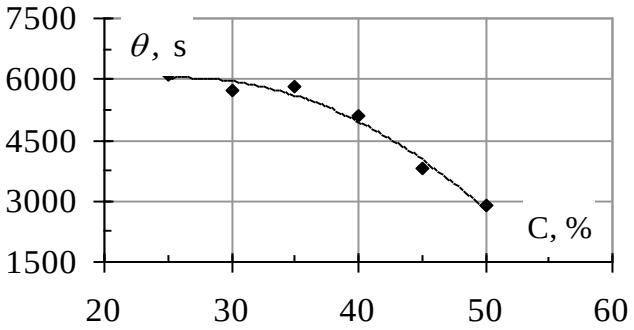


Figure 4.50 The dependence of the relaxation of the snack paste model system on lactic acid curd content

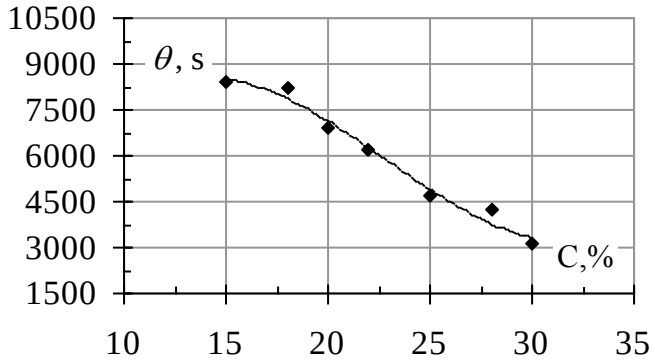


Figure 4.51 The dependence of the relaxation of the snack paste model system on vegetable oil content

The relaxation period characterizes the rate of the process, i.e. the transition of the system from unbalanced thermodynamic state caused by outside effects to the state of thermodynamic equilibrium [27, 81, 83]. During this time with 30…40% lactic acid curd concentration increase in the recipe of the pastes' model system the strain decreases almost 1.2 times; with 20…25% vegetable oil concentration increase in the recipe of the pastes it decreases almost 1.3 times; 1.2…1.4% agar concentration increase in the recipe of the pastes' model system it increases almost 1.5 times (Table 4.8).

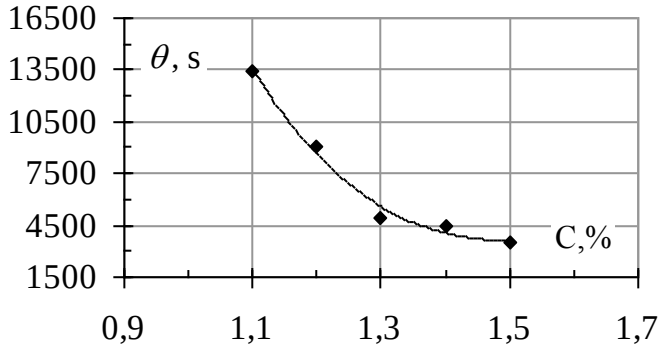


Figure 4.52 The dependence of the relaxation of the snack paste model system on agar content

In 30….40% lactic acid curd concentration range in the recipe the relaxation time of the pastes' model system decreases by 1000±10 s. When lactic acid curd content is 40±2%, it is 5000 s. In 20….25% vegetable oil concentration range the relaxation time of the pastes' model system decreases by 2500 s. When vegetable oil content is 25±2%, it is 4800 s, which demonstrates the increase of plastic properties and the decrease of spring properties. So, it positively affects the mixing and prepacking conditions. In 1.1….1.3% agar concentration range the relaxation time of the pastes' model system increases by 3500 s. When agar content is 1.4±0.1%, it is 8500 s, which demonstrates the increase of elastic and spring properties, and the decrease of plastic properties. So, it negatively affects the mixing and prepacking conditions [27, 92].

4.5. Investigating the Changes of Fractional Composition of the Protein Complex in the Snack Pastes' Model System

Taking into consideration the incompatibility of thermodynamic processes taking place in milk protein and agar during thermal processing and structure formation, we have investigated the structure formation process of the model system of the snack pastes on the base of fat-free lactic acid curd due to protein-polysaccharide interactions, which can cause the change of their molecular masses. Thus, in the framework of this research we have investigated the changes of the fractional composition of proteins of the model system before and after thermal processing (Table 4.12), as well as the molecular mass changes in protein substances [93, 94] during the structure formation (Figure 4.53).

Table 4.12 – The change of nitrous substances content in the snack pastes' model system during structure formation

Attribute	Snack paste model system			
	before thermal processing		after thermal processing	
	content, %	of N_{total},%	content, %	of N_{total},%
Mass part of DDMR	14.5	–	15.4	–
Total nitrogen (N_{total}),	9.7	100	9.2	100
including: protein nitrogen	8.9	91.75	8.7	94.57
nonprotein nitrogen	0.8	8.25	0.5	5.43

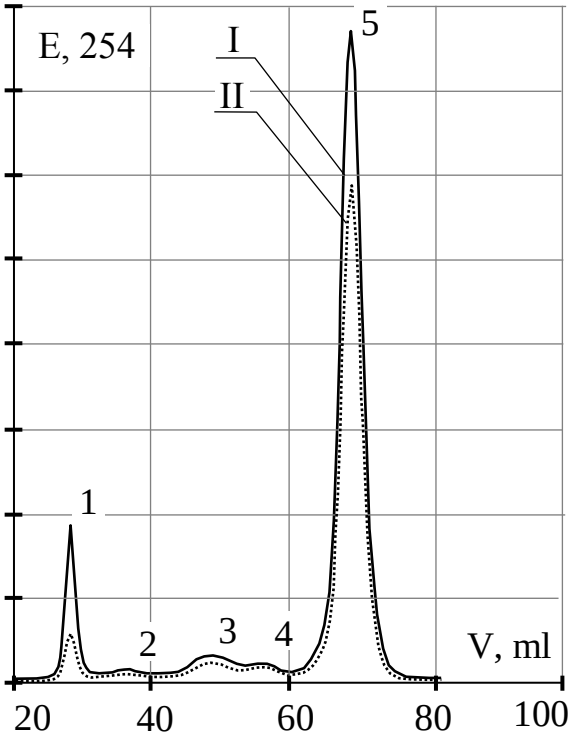


Figure 4.53. The chromatograms of protein-polysaccharide interaction of the snack paste model system on the base of fat-free lactic acid curd (I - without agar, II - with agar): 1 – immunoglobulins, 2 – a_s-casein, 3 – β- casein, 4 – χ- casein, 5 – β-lactoglobulin

The analysis of Table 4.12 shows that 91.75% of nitrous substances in the snack paste model system are represented by protein nitrogen. The percentage of nonprotein nitrogen is 8.25% of the total nitrous substances content. After thermal processing the percentage of total nitrogen of the paste model system decreased by 0.50%, which is an uncertain value. There no significant observed changes in redistribution of protein and nonprotein nitrogen. So, in general, the process of iontropic gel formation does not affect the content of protein substances, cause undesirable changes, the outcome of which is their insignificant loss.

However, the data concerning the change in the total amount of nitrous substances do not give full information about the qualitative and quantitative transformations of protein fractions of the snack pastes' model system before and after thermal processing.

We may assume that the structurization in these systems can go on because of iontropic structurization due to sodium citrate's action (Figure 4.13), as well as because of formation of protein-protein and protein-polysaccharide complexes through affinity with the help of a relevant solvent.

At the same time, with the objective of confirming this hypothesis we have investigated the snack pastes' model system to define proteins' molecular masses

by the gel-chromatography method (Figure 4.53). We have identified the protein components of the snack pastes' model system without agar with molecular masses: ~1000000 Da (13.89%) – immunoglobulins, ~25000 Da (0.29%)– a_s-casein, ~24000 Da (4.8%) – β-casein, ~19000 Da (2.17%) – χ-casein, ~18000 Da (78.8%) – β-lactoglobulin.

The protein components' content has somewhat changed in the structured snack paste model system with agar. The percentage of high-molecular fraction (immunoglobulins) has decreased by 8.68% and is 5.21%, while the percentages of low-molecular fraction have increased and are: 2.04% of a_s-casein, 6.52% of β- casein, 3.34 of χ- casein, 82.9% of β-lactoglobulin.

Obviously, owing to the sorption of the part of proteins on its surface agar transforms them into a weakly soluble form constructing a structural grid. As a result, after re-suspension in phosphate-salt buffer and centrifugation of protein gel sedimentary protein complexes transform into sediment, while fully soluble proteins, whose concentration lowers remain in supernatant. The correlation of fractions accordingly changes.

A significant increase of the part of low-molecular fractions, especially χ- casein and β-lactoglobulin, will contribute to their sorption on high-molecular fractions giving the latter increased stability in water solutions and to the increase of water bondage, which conforms to the results of the previous research (Figure 4.37…4.41, 4.44).

4.6 Investigating the Influence of the Ratio of the Main Components in the Snack Pastes' Model System on Organoleptic Attributes

According to the classification of food products' structures proposed by P.A. Rebinder, taking into consideration the snack products' water content, they may be classified as disperse systems with structures of coagulation or coagulation-condensation type. The snack pastes on the base of fat-free lactic acid curd with a rather high water content, which being a disperse environment forms interlayers between protein particles and molecules, are the coagulation-type structures. They interact through these interlayers mostly by Van der Vaals binding forces [27, 52, 54, 59].

The structure of the snack paste model system on the base of fat-free lactic acid curd may be presented in simplified form as a three-dimensional netlike protein grid with fairly equally distributed water and fat. Proteins provide for strong, resilient and

elastic properties of the paste model system, fat affects plasticity, and water affects viscosity.

So constructed spatial protein grid of the snack paste model system is not strong. Thixotropy – the ability to renew quickly after breaking – is its characteristic feature. Moreover, its consistency changes from soft, plastic, a little elastic to tender, slightly fluid. On ruining the structure restores after some period of time. The shorter this period, the more water is contained in the recipe.

When water content in the snack paste model system decreases, the thickness of water interlayers between protein particles diminishes. This creates other more powerful forces compared to Van der Vaal's forces of interaction between the fragments of protein molecules. I this case he strength of the structure grows. The thixotropic properties partially remain, but the time necessary to restore after ruining increases significantly. When a certain defined limit of moisture content in the recipe is reached, the spontaneous ability of restoring the structure after its ruining is lost. Now to restore the broken bonds it is necessary to apply additional strain, which causes plastic deformations. Further reduction of water amount in the snack paste model system causes qualitative structural changes. It transforms from coagulation-type into coagulation-condensation-type, which differs from the former by greater strength and elasticity, a lack of thixotropy, a chance of graininess [27, 52].

The experimental research has established that the chemical composition of the snack paste model system may also vary within the scientifically grounded values: protein content – 7.4…12.5 %, moisture – 54…68%, fat in solid – 40…60%.

The changes of these indices' ranges let adjust the texture characteristics of the finished product. Proteins comprise the base (80%) of dry defatted milk residual (DDMR). The other part of DDMR is comprised by mineral salts. Such composition make it possible to regard the model system as a three-component physical-chemical system. We made a graphic presentation of the model system in linear approximation (Figure 4.54). Nonlinear effects depending on the main components concentrations will be accounted for further (Figure 5.13, 5.14).

The state of three-component systems is determined (at constant pressure and temperature) and by two variables: concentrations (%) of mass particles of fat and water. The third component's (DDMR) concentration is defined from the condition $z=100-(x+y)$.

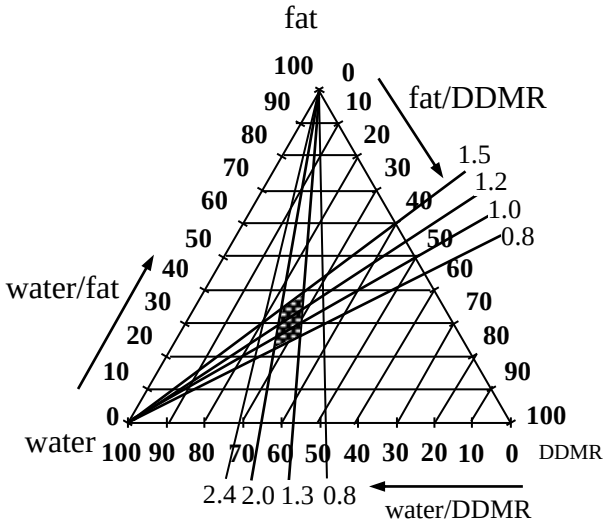


Figure 4.54. The correlation water-DDMR of the model system the snack paste on the base of fat-free lactic acid curd

The dependence of the changes of the snack paste model system on the correlation of the main recipe components has been established on the basis of the research of the dependence of threshold shear strain of the model system on moisture content (Figure 4.55) and the organoleptic investigations of consistency (Figure 4.55), using the known in physical chemistry method of analysis of three-component systems' composition (the concentration triangle method) (Figure 4.56) [13]. The consistency, which at 60% vegetable oil concentration in the paste model system's solid corresponds to water/DDMR correlation within 0.8…1.3 is defined as dense with threshold shear strain 260…240 Pa, to water/DDMR correlation within 1.3…2.0 defined as tender, plastic with threshold shear strain 240…170 Pa, to water/DDMR correlation within 2.0…2.4 defined as spreading, fluid with threshold shear strain 170…110 Pa.

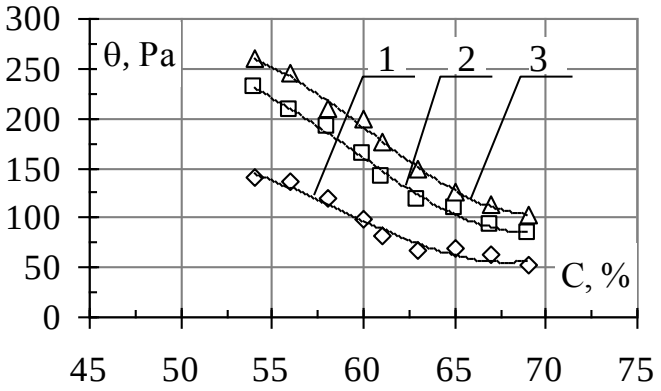


Figure 4.55. The dependence of threshold shear strain of the snack paste model system with vegetable oil contents in DDMR: 1 – 40%, 2 – 50%, 3 – 60% on moisture

The consistency, which at 40% vegetable oil concentration in the paste model system's solid corresponds to water/DDMR correlation within 0.8…1.3 is defined as rough with threshold shear strain 150…120 Pa, to water/DDMR correlation within 1.3…2.0 defined as plastic, fluid with threshold shear strain 120…80 Pa, to water/DDMR correlation within 2.0…2.4 defined as gel-like with threshold shear strain 80…50 Pa.

The investigations of threshold shear strain of the snack paste model system with different vegetable oil contents in solid (Figure 4.55) have established that the increase of moisture within 54…68% in the model's recipe with 40±3% vegetable oil concentration causes the lowering of threshold shear strain by 88±5 Pa, with 50±3% vegetable oil concentration – by150±10 Pa, with 60±3% vegetable oil concentration – by160±10 Pa. When water content in the model system is 55±3%, the increase of vegetable oil concentration in solid within 40…50% causes the heightening of threshold shear strain by 90±5 Pa, within 50…60% - by 40±3 Pa. When moisture percentage is increased to 65±3% these indices reduce 2 times and attain 40±3 Pa and 20±2 Pa.

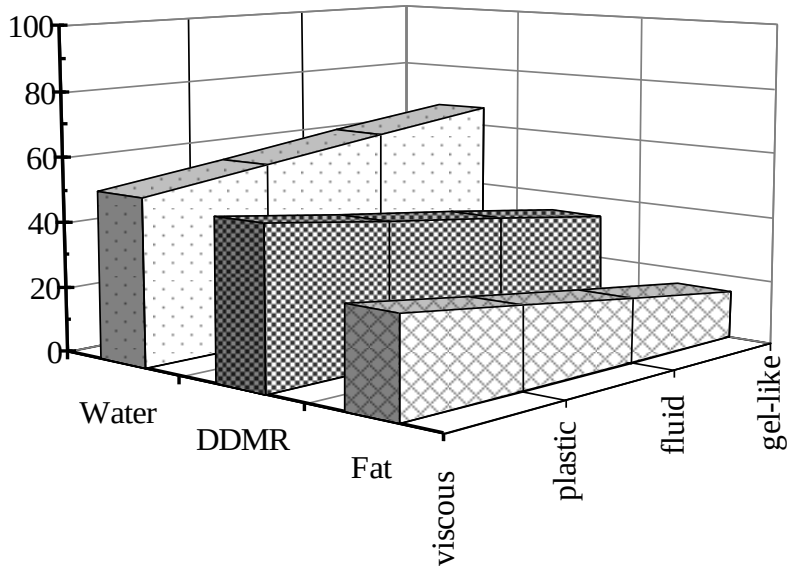


Figure 4.56. The effect of water/DDMR correlation on the snack paste model system's consistency

The organoleptic investigations of the consistency of the snack paste model system (Figure 4.56) have established that the insufficient amount of fat in the system does not provide for the required weakening of protein molecules' bonds, which results in rough product consistency. A significant water content increase does not cause positive outcomes, because it gives the product excessive viscosity, which from the point of view of organoleptic is regarded as "stickiness", and increases fluidity of the structure, makes it very similar to gel [12, 27, 49, 59]. The

excessive amount of fat in the system with insufficient amount of moisture raises its plasticity and elasticity, makes it viscous and transforms it from paste-like into slice-like.

Thus, it will possible to adjust the consistency of snack pastes of the emulsion type with the properties characteristic of this product by varying the correlations of water phase and solids within 0.8…2.4 and purified deodorized vegetable oil content in solid within 40…60% [12, 27, 49]. The additional increase of the adjustment range of rheological characteristics of the snack pastes giving them the required organoleptic properties is provided for by adding 1.3±0.1% of agar to the recipe as structure former.

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Chapter 5. Development of the Technology of the Pastes on the Base of Fat-free Lactic Acid Curd

5.1. Working out the Recipe and Technology of the Snack Pastes

The scientific substantiation of the recipe (Table 5.1) normatively recorded in the worked out and approved Ukrainian specification ТУ У 15.5-01566330-190:2006 "Snack Pastes from Lactic Acid Curd", the technology and flowchart (Figure 5.2) of the pastes on the base of fat-free lactic acid curd has been fulfilled on the basis of the complex experimental research of the main recipe components, the model system and the finished product.

The model flowchart of the snack pastes production has been worked out as a technological system to define the recipe composition with the objective of safeguarding the principal regularities of the technological process. With the help of the decomposition-aggregation method the functional components of the system can be defined as separate subsystems A, B, C, D (Figure 5.1).

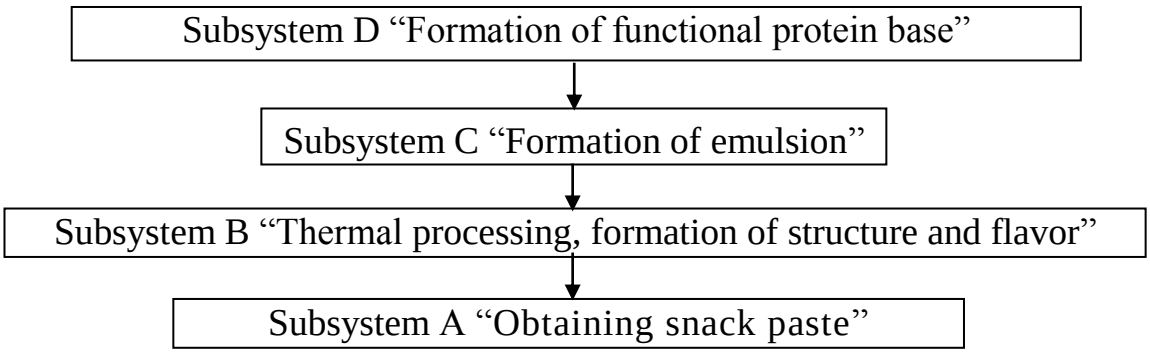

Figure 5.1 Model flowchart of snack paste production

The model has been built based on the synthesis of functioning and interactions of each subsystem governed and provided for by the results of the performed research (sections 4.1…4.6).

The basic criteria of functioning of the model flowchart of snack paste production are high organoleptic and physical-chemical indices, consumer safety, and nutritional value of the finished product [1].

To substantiate the technological (Figure 5.2) stages we decomposed the worked out model flowchart of snack paste production on the base of fat-free lactic acid curd (Figure 5.1) as an integral technological system into the following subsystems: subsystem A "Obtaining snack paste" is formed as a result of the synthesis of subsystem B "Thermal processing, formation of structure and flavor."

Table 5.1 – Composite recipe of snack pastes makes 100 kg

Ingredients	Mass part of solid, %	Total consumption of raw materials, including losses during technological process, kg	
		in natural product	in solids
Fat-free lactic acid curd	26	40	10.40
Defatted dry milk	95	4	3.80
Purified deodorized vegetable oil	99.9	25	24.98
Sodium citrate	96	2	1.92
Common salt	96.5	0.27	0.26
Sodium dioxide	50	0.26	0.13
Agar	94	1.3	1.22
Potassium sorbate *	95	0.1	0.10
Aromatizer identical to natural Butter Buds Food Ingredients:			
«Cheese»	96	0.5	0.48
«Mushrooms»	96	0.5	0.48
«Bacon»	96	0.5	0.48
Water		29.36	–
Total		102.79	43.28
Output		100	43.28
*Used for prolonged storage products			

Further, subsystem B forms in the synthesis of subsystem C “Formation of emulsion,” which is dependent in hierarchy on subsystem D “Formation of functional protein base.” Thus, to research and scientifically substantiate the technological stages of the snack pastes production taking into consideration that the existence of this technological system in general is ensured by the functioning and hierarchal dependence of its separate subsystems A, B, C, D, we decomposed them into separate tasks (Figure 5.2) within these subsystems. Fulfillment of these tasks ensures the overall fulfillment of the main objective of the system [2, 3, 4].

Subsystem D “Formation of functional protein base” provides for the change of milk protein’s functional-technological properties: the increase of moisture retaining capability, increase of hydration properties, the increase of its buffer capacity by acting on fat-free lactic acid curd’s active acidity by sodium dioxide,

which plays the role of a corrector of active acidity, and by melting salt – sodium citrate, which insures the necessary ion exchange in the protein base.

Table 5.2 – Structure and tasks of component parts of technological system

Subsystem		Task of subsystem
Letter symbol	Name	
A	Obtaining snack paste	Obtaining snack paste with paste-like plastic structure capable of retaining set properties during storage due to the functional functional-technological properties of main ingredients.
B	Thermal processing, formation of structure and flavor	Substantiation of the temperature and duration of thermal processing, substantiation of concentration of agar – the main structure-forming component, substantiation of concentration of flavoring-aromatizing ingredients.
C	Formation of emulsion	Substantiation of concentration of purified deodorized sunflower oil, lowering of the thermal processing temperature, increase of plastic and decrease of elastic properties. Increase of nutritional value of the finished product.
D	Formation of functional protein base	Providing for the increase of moisture retaining capability of lactic acid curd protein, improvement of its solubility, increase of hydration properties, and increase of its buffer capacity.

We have experimentally found the rational value of acidity pH 5.8…6.2, which ensures the necessary conditions for milk protein hydration; rational values of sodium dioxide concentration 0.4±0.1%, and sodium citrate concentration 2±0.2%, which provide for 75±2% increase of protein's MRC due to the decrease of the amount of "free" water in the recipe mixture (Figure 4.11, 4.12, 4.37, 4.38, 4.43) positively affect the process of preparation for thermal processing (Figure 4.5, 4.7) and do not negatively affect flavor attributes of the snack pastes. The aging duration of the snack paste protein base, which is (28±2) ×60 s, plays an important role in the process (Figure 4.10). The ruining of "calcium bridges" in milk protein due to the

hydrolysis of sodium citrate takes place during this time (Figure 4.5, 4.9). Protein's solubility improves (Figure 4.1) and hydration increases (Figure 4.5, 4.7).

Subsystem C "Formation of emulsion" provides for forming of protein-fat emulsion, which affects the thermal processing temperature, the duration of structure formation, structural-mechanical attributes, raises nutritional value of the snack pastes.

It has been found that 40±2% fat-free lactic acid curd content provides for the emulsification ability of the protein base within 32±1 volume units, the addition to the recipe of 6±0.5% of dry defatted milk increases the emulsification ability to 52±2 volume units, 2±01% of sodium citrate insures 50±2 volume units emulsification ability of the protein base.

It has been experimentally proved that the thermal processing at 80 ± 2^0C contributes to the increase of kinetic stability. It attains 95±2% when the content of fat-free lactic acid curd is 40±2% and the content of vegetable oil is 25±2%. The aggregate stability of the snack paste model system is 96…98%.

Taking into consideration modern trends concerning fat and cholesterol contents in human nutrition, the research within the subsystem framework were aimed at determining the possibility of complete substitution of milk fat by purified deodorized sunflower oil, the substantiation of its concentration in the recipe of the snack paste recipe within 25…35%, and defining the finished product's nutritional value.

Subsystem B "Thermal processing, formation of structure and flavor" due to the temperature effect, sodium dioxide and sodium citrate action [5, 6, 7], the addition of agar [88, 9, 10, 11, 12] as stabilizer, 0.5±0.01% of Butter Buds Food Ingredients aromatizer [13, 14…16], and intensive mixing provide for the stabilization of the structure, formation of the texture, and flavor attributes of the finished product.

This subsystem's tasks were fulfilled by heating the prepared protein-fat emulsion at 80 ± 2^0C.

It has been experimentally established (Figure 4.26…4.28) that fat-free lactic acid curd and agar raise the thermal processing temperature, while vegetable oil lowers it. On the whole, the main components' contents: 40±2% of fat-free lactic acid curd, 25±2% of vegetable oil, 1.3±0.1% of agar provide for the thermal processing temperature of 80 ± 2^0C.

The addition of 1.3±0.1% of agar to the recipe provides for the high level of binding of macromolecules, the formation of the structural grid (Figure 3.43), reduces water loss during the thermal processing by 6 ±0,5% (Figure 4.35, 4.36).

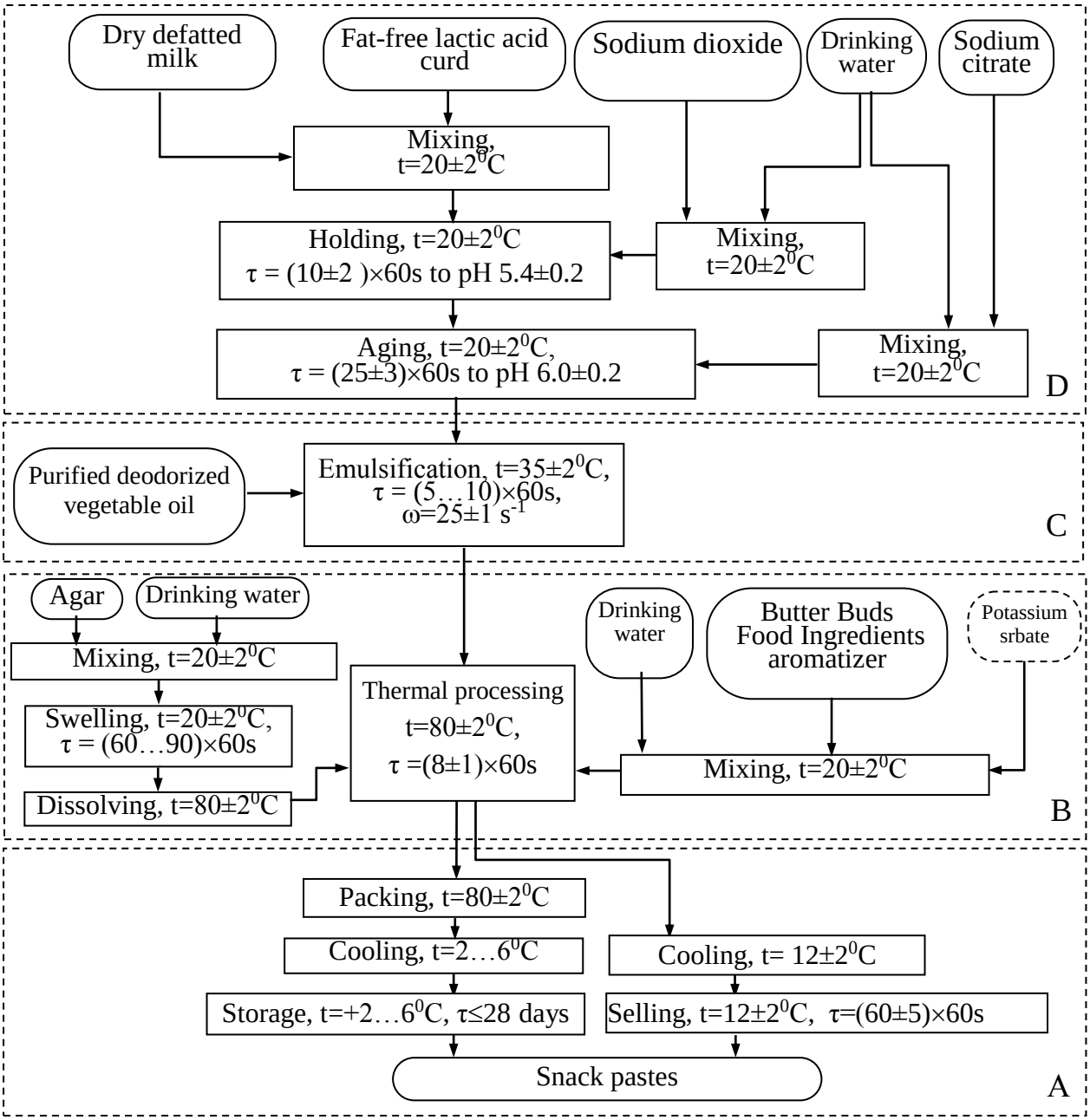

Figure 5.2 Technological flowchart of production of snack pastes on the base of fat-free lactic acid curd

It has been established (Figure 4.40, 4.41) that (8±2)×60 s is the rational thermal processing duration, and further heating during (2±0.5)×60 s causes unnecessary loss of moisture by ~15±3%.

Mathematical modeling (Figure 4.44…4.46) determined the values of the main components of the snack pastes: 40±2% of fat-free lactic acid curd, 25±2% of

vegetable oil, 1.3±0.1% of agar and the thermal processing temperature within 80 ± 2^0C.

The addition of agar to the paste recipe is based on its attribute of swelling and form colloidal solutions of high viscosity in hot water, which result in strong gels during cooling even at a low concentration due to the formation of the structural grid (Figure 4.39), which are capable of significantly raising the finished product's resistance to ruining. Moreover, agar contributes to ordering the structure (Figure 4.37, 4.38, 4.43, 4.49), shortens the structure formation duration (Figure 4.31), raises the snack pastes' thermal processing temperature (Figure 4.28, 4.35, 4.36).

The addition of aromatizer to the recipe of the snack pastes is necessary to give them specific organoleptic attributes.

Subsystem A "Obtaining snack paste". To fulfill the subsystem's tasks the homogenized melted paste at 80 ± 2^0C was put into consumer containers and cooled down to 18 ± 2^0C. The cooled pre-packed product was kept for 28 days at $+2\ldots6^0$C [17].

5.2. Investigating Physical-Chemical Characteristics of Snack Pastes during Storage

5.2.1 Structural-Mechanical Changes

Storage is one of the important stages, which affects the finished product quality. This the reason why it is necessary to investigate the influence of storage modes and shelf-life durations on quality attributes of the snack pastes.

To determine the rational storage term at $+2\ldots6\ ^0$C we have investigated the structural-mechanical changes of freshly-made snack pastes kept packed for 35 days (Figure 5.3), defined the total deformation, viscosity, relative elasticity, plasticity, spring, relaxation period (Figure 5.3) [18, 19, 20, 21].

It is worth mentioning that the storage conditions for the snack pastes on the base of lactic acid curd have been selected taking into consideration the storage requirements for the products of this kind.

The analyzed snack pastes' creep curves (Figure 5.3) have shown that the most fluid sample is the first day of storage sample with total deformation $225.0\cdot10^{-3}$. After seven days of storage total deformation (Table 5.3) decreases insignificantly to $191.0\cdot10^{-3}$, which is confirmed by insignificant increase of conditionally instant coefficient of elasticity (Figure 5.4). During further storage of the pastes total deformation decreases slowly, 1.1 times on the average, and attains $121.0\cdot10^{-3}$ on day 28.

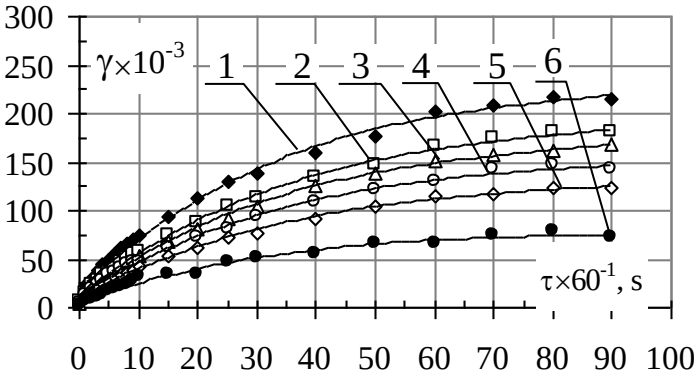

Figure 5.3 Creep kinetics of snack paste during storage, days: 1 – 1; 2 – 7; 3 – 14; 4 – 21; 5 – 28; 6 – 35

Thus, we may assume that during storage there is an insignificant increase of density of the finished product, which is confirmed by an insignificant increase of conditionally instant coefficient of elasticity and slow insignificant increase of the coefficient after 21 days of storage.

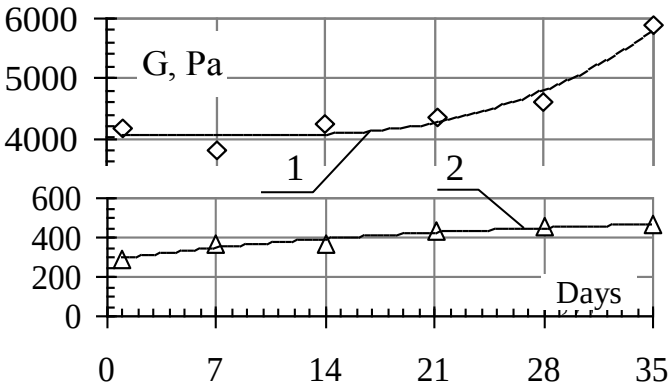

Figure 5.4. Dependence of conditionally instant coefficient of elasticity (1), high elasticity coefficient (2) of snack pastes on storage term

The analysis of the graphs (Figure 5.4) of the dependences of the coefficients on storage term has shown that after 14 days of storage the conditionally instant coefficient of elasticity keeps the tendency towards an insignificant gradual increase by ~120±10 Pa during the next term. At the same time the high elasticity coefficient grows each 7 days by ~10±2 Pa only (Table 5.3). After 28 days of storage a sharp increase of the high elasticity coefficient is observed, which is up to 5800±10 Pa on day 35 and characterizes the loss of plastic properties of the structure.

The calculations of relative plasticity, spring and elasticity of the finished product (Figure 5.5) confirm that during storage to 21 days the plastic attributes of the pastes remain on the same level.

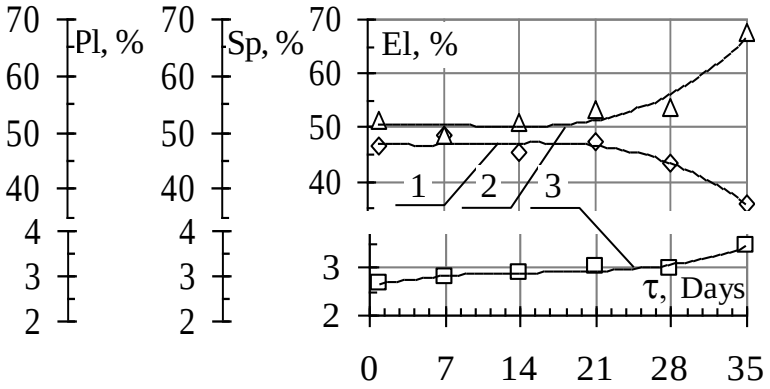

Figure 5.5. Dependence of relative plasticity (1), spring (2), elasticity (3) on snack pastes' storage term

However, during further 7 day storage they decrease by 10±2% and do not deteriorate the organoleptic attributes of the finished product. The product's spring does not change during the first 14 days, and each 7 days of the further 14 day period it has the tendency towards gradual increase by 6±2%, i.e. it increases by 18% on day 35 and considerably affects the organoleptic attributes.

Table 5.3 – Structural-mechanical characteristics of snack pastes during storage

Symbols	Name of attribute	Term of storage, days					
		1	7	14	21	28	35
$\gamma_{rev.}$	Reversible deformation, 10^{-3}	113.20	101.29	87.64	78.71	72.65	68.60
$\gamma_{irr.}$	Irreversible deformation, 10^{-3}	111.80	89.71	75.86	64.29	48.35	32.58
γ_{total}	Total deformation, 10^{-3}	225.00	191.00	163.50	143.00	121.00	98.00
P	Shear strain, Pa	32.70	32.70	32.70	32.70	32.70	32.70
I	Compliance, Pa^{-1}	$6.9\cdot10^{-3}$	$5.8\cdot10^{-3}$	$5.0\cdot10^{-3}$	$4.4\cdot10^{-3}$	$3.7\cdot10^{-3}$	$2.2\cdot10^{-3}$
$G_{el.}$	Conditionally instant coefficient of elasticity, Pa	4241.25	4342.50	4450.00	4510.75	5010.72	5620.00
G_{el}	High-elasticity coefficient, Pa	309.27	342.14	394.56	436.58	470.84	510.62
η	Viscosity, Pa×s	$9.86\cdot10^{5}$	$1.94\cdot10^{6}$	$2.31\cdot10^{6}$	$2.71\cdot10^{6}$	$3.60\cdot10^{6}$	$4.80\cdot10^{6}$
K	Deformation ratio ($\gamma_{rev.}/\gamma_{total.}$)	0.52	0.53	0.54	0.55	0.60	0.70
El	Relative elasticity, %:	2.11	2.99	2.91	2.66	2.64	4.28
Pl	Relative plasticity, %:	48.47	46.97	46.40	44.96	39.96	30.24
Sp	Relative spring, %:	49.42	50.04	50.69	52.38	57.40	63.56
Θ	Relaxation period, s	5671.36	5999.41	6186.35	6513.93	7998.17	8436.54

After 28 days during the next 7 days relative plasticity decreases by 12%, while relative spring increases by 15%. Relative elasticity increases by 1±0.2 Pa

after 28 days. It has no significant effect on the organoleptic attributes of the pastes.

Thus, during the snack pastes' storage for 21 days the product's relative spring, plasticity and elasticity do not significantly change (Figure 5.5). Significant changes of spring and plasticity take place during the last 7 days of 28 day storage. Further storage after 28 days is not rational and may cause significant deterioration of plastic and increase of spring attributes, probably, due to protein's and agar's effect on re-distribution of moisture, which may cause the deterioration of organoleptic attributes.

5.2.2 Changes of Active Acidity

The snack pastes' active acidity significantly characterizes flavor attributes of the finished product. This is the reason why it is important to determine pH value during the whole storage term [22].

During the research we determined the kinetics of active acidity changes of the snack pastes on the base of lactic acid curd within the defined 28 day storage term (Figure 5.6) and compared it to the control samples: control-1 – "Khreshchatyk" snack paste, control-2 – "Yantar" melted cheese.

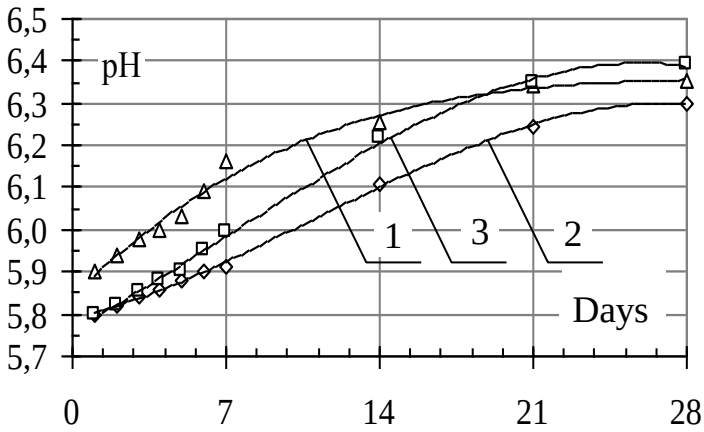

Figure 5.6. Change of active acidity during storage: 1 – snack paste, 2 –control-1, 3 – control-2

The active acidity in the snack paste and control samples grows during storage towards neutrality from pH 5.9 to 6.0, in freshly-made samples it grows to pH 6.2…6.3 on day 28 of storage. Thus, we may conclude that during the 28 day storage term the manufactured product tends to change its active acidity similarly to the control samples, which are in demand with consumers.

5.2.3 Investigating Moisture Loss

The experimental research in loss of moisture, which has different forms of binding with protein, has been performed on the basis of the analysis of the mass change curves (TG), differential thermogravimetry (DTG and DTA) and temperature (T) (Figure 5.7).

It has been established that the mass loss due to moisture loss during storage of snack pastes goes on endothermally, which is recorded on DTG and DTA curves, in three stages in the freshly-made product and in two stages in the finished product after 28 days of storage [1, 18, 23, 24].

During heating of a freshly-made sample the temperature interval of 55…58^{0}C (range I – the beginning of polymorphic changes of protein) is characterized by a weak endothermic peak, which reflects thermal processes, which go on in the paste during the intensive release of water due to the thermal effect with 16.6% mass loss. This may be weakly bound water present in the system's micropores.

The freshly-made sample's temperature interval of 80±2^{0}C (range II – the main thermal processing range) is characterized by an endothermic peak, which reflects thermal processes going on at the end of the processing, and mark the increase of protein's hydration ability under the temperature effect and a partial water release weakly bound with protein. The intensity of water release is ~59.6%.

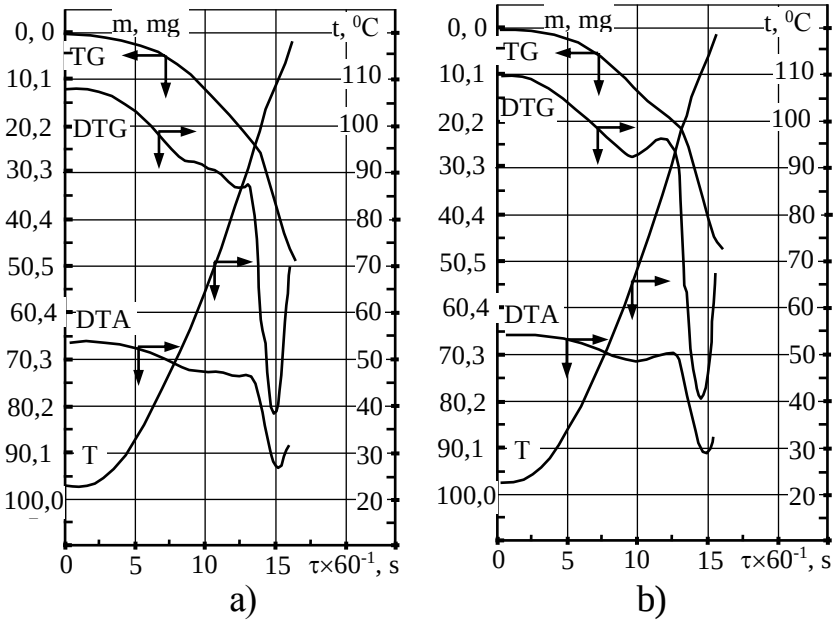

Figure 5.7. Dependence of mass loss (TG), mass loss rate (DTG), thermal effects (DTA) under non-isothermal conditions on duration of snack pastes' thermal processing: a –freshly-made paste; b – after 28 day storage

During heating of the sample having been stored for 28 days there are polymorphic changes in the protein system, which are characterized by an endothermic peak at 80±2^{0}C in the main thermal processing range, which reflects

thermal processes going on at the end of the processing, and mark the increase of protein's hydration ability under the temperature and agar effect on retaining water weakly bound with protein by the structural grid. In this case, the moisture loss is around 27.5%. At 90±3 ^{0}C it is 37.5%, which is 22.7% less than in the freshly-made sample.

A sharp endothermic peak was observed in the temperature interval of 110…115 ^{0}C (range III – destructive changes) both in the freshly-made sample and the sample after storage, which reflects thermal processes going on in the paste during ruining carbohydrates' and proteins' structure with gas-like fractions release.

Thus, the investigations have confirmed that during the storage of the snack pastes during 28 days there is a slight ordering of the finished product's structure, which prevents moisture loss due to the re-distribution of moisture because of protein and agar interaction.

5.3. Investigating the Nutritional and Biological Value of the Snack Pastes on the Base of Fat-free Lactic Acid Curd

The nutritional value of food products is defined by their protein, fat, carbohydrate, mineral and vitamin content. The nutritive content within the developed assortment of snack pastes will be specific to each item. However, the fluctuations of the absolute values of their attributes will be insignificant. This the reason why we assume it possible to perform our investigations of nutritional values and their change under effects of various technological agents using the snack pastes on the base of lactic acid curd as a test sample.

Proteins' biological and nutritional value is an integral attribute, which is defined by the quality and quantity of protein in a diet, protein's digestibility by gastrointestinal tract's proteinases, rate of absorption of amino acids and their utilization to satisfy human organism's requirements[27…31].

It is known that fat-free lactic acid curd proteins have a high biological value, which is defined by both their amino acid composition and their digestibility and metabolic transformations of exogenous amino acids, which have been absorbed.

Casein, the main lactic acid curd protein, which is the base of the snack pastes, has a number specific properties contributing to its adaptation to digestion process [27, 32…34]:

- first, it is the ability to precipitate (i.e. to form clots in acid medium) under the effect of some proteinases, as well as in the presence of ions of calcium;

- second, casein is one of the proteins, which form complex aggregates called micelles in solution;
- third, casein can be well hydrolized by proteolytic enzymes, which allowed some researchers to compare this protein's hydrolysis to globular proteins in denatured state [25, 29, 35, 36];
- fourth, casein differs from globular proteins in some physical-chemical properties and chemical composition (Table 5.4).

The nutritional value indices were defined with the help of known methods [25, 35, 36].

The fat-free lactic acid curd-based snack pastes' total chemical composition (Table 5.3) and nutritional value (Table 5.5…5.7) were defined by their protein, fat, vitamin and mineral content.

Table 5.4 –Total chemical composition of snack pastes

Components	Content, %
Mass part of moisture	58.7±1.0
Mass part of solids	43.3±1.0
Mass part of proteins	8.7±03
Mass part of fat	26.9±0.5
Mass part of carbohydrates	2.8±0.1
Mass part of sols	4.9±0.5

It is worth mentioning while analyzing the chemical composition (Table 5.4) that we have found 8.7±0.3% of protein substances, which provided by the main protein-containing recipe components – fat-free lactic acid curd and dry milk and comprise 17.6 % of the total solid content.

From the point of view of biological value, besides the total protein content in the product, its quality is of great importance and is the most importantly characterized by the content and the ratio of essential amino acids.

To determine the biological value of the snack pastes on the base of fat-free lactic acid curd we defined its amino acid composition (Table 5.5).

Table 5.5 –Amino acid content of snack paste

Amino acid	Content	
	mg/100g	%
1	2	3
valine	492.24	5.62
isoleucine	371.55	4.24
leucine	734.43	8.38

1	2	3
lysine	328.62	3.75
methionine	2302.4	2.65
threonine	331.58	3.79
tryptophane	85.6	0.98
phenylalanine	310.83	3.55
Essential amino acids, total	2887.25	32.96
asparagine	656.46	7.49
serine	639.47	7.30
glutamine	1667.51	19.04
proline	1108.82	12.66
cystine	78.44	0.90
glycine	246.63	2.82
alanine	558.28	6.37
tyrosine	302.81	3.46
histidine	198.94	2.27
arginine	414.48	4.73
Nonessential amino acids, total	5871.84	67.04
Total	8759.09	100

During the research (Table 5.6) we have identified and determined quantitative values of 18 amino acids. The total essential amino acid content is 32.96%. It lets us characterize the snack paste on the base of fat-free lactic acid curd as a product of high biological value.

The snack pastes' amino acid composition in regard to protein's biological value was estimated by comparing with the amino acid composition of the FAO/WHO reference protein and calculating the amino acid score (Table 5.6).

Table 5.6 – Amino acid score of proteins of snack pastes

Amino acid	Amino acid content in protein, mg/g		Score, %
	FAO/WHO	Paste	
leucine + isoleucine	110	118	107
lysine + histidine	55	55	100
valine	50	52	103
tryptophane	10	10.1	101
threonine	40	40	100
phenylalanine + tyrosine	60	61	102
methionine + cystine	35	35.2	101

The analysis (Table 5.6) shows that the snack paste does not exceed the FAO/WHO limits of amino acid contents. Limiting amino acids are absent.

Against this background we can see an insignificant excess of leucine and isoleucine.

Not only the presence of essential amino acids, but also their balance is an important index of a fully biologically valuable protein. To estimate the threonine and tryptophane levels in the snack pastes, which characterize the amino acid equilibrium, we have calculated the threonine and tryptophane indices (Table 5.7).

Table 5.7 – Balance of essential amino acids in the snack pastes composition

Amino acid	Tryptophane index balance		Threonine index balance	
	FAO/WHO scale	snack paste	FAO/WHO scale	snack paste
threonine	2…3	4,0	1	1
lysine + histidine	3…5	5.5	1.1	1.37
valine	4	5.1	1.5	1.28
leucine + isoleucine	7…10	11.7	3.1	3.0
phenylalanine	2…4	3.7	1.1	1.0
methionine	2…4	2.5	0.7	0.62
tryptophane	1	1.0	0.25	0.25

The analysis of the ratio by tryptophane index shows that the snack paste has excessive isoleucine and valine. However, it has a good balance of lysine, phenylalanine, and methionine. The analysis of the ratio by threonine index shows that the snack paste has excessive lysine. However, it has a good balance of valine, isoleucine, leucine, and tryptophane.

Thus, the summed up results of the research shoe that the snack paste on the base of fat-free lactic acid curd is a source of fully valuable protein, mostly balanced in its amino acid composition.

The amino acids' availability is affected by a number of factors mostly relating to their incomplete digestion, which is observed when there are cross bindings in a protein molecule due to the presence of inhibitors of protease, as well as peptides and peptide-like compounds inhibiting amino acids' absorption [28…30].

The amino group content in the samples was defined with the help of calibration graphs by Lowry method, which is based on the formation of colored products during the interaction of Folin's reagent with alkaline solutions of

proteins (Appendix K.2). Color intensity depends on tryptophane and tyrosine amino acid content in thee researched protein.

During the experiments the degree of proteolysis in milligrams of tyrosine per 1 mg of protein in the product (Figure 5.8) was determined. The results of the experimental research confirm that the digestion of the snack pastes' protein goes in two stages (Figure 5.9).

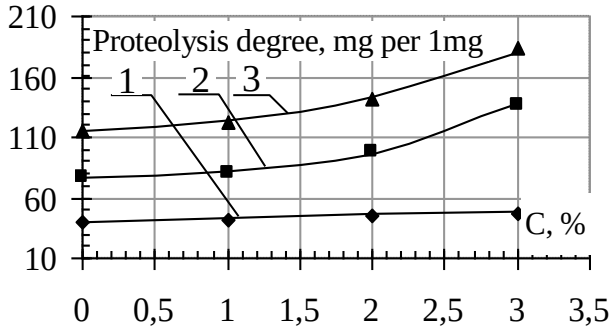

Figure 5.8. Dependence of hydrolysis of the snack pastes' protein by proteases: 1- pepsin, 2-tripsin, 3-total on sodium citrate content

The degree of hydrolysis of casein in fat-free lactic acid curd in the processed snack paste depending on sodium citrate content in the recipe does not significantly change under pepsin's action (40…46 mg). However, due to the combined action of pepsin + tripsin proteases casein acquires significant hydrolysis ability (122…183 mg) not only with the increases of sodium citrate concentration in the recipe, but also in native state (116 mg) in lactic acid curd.

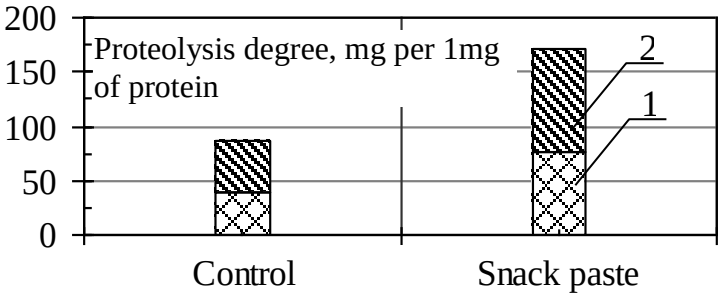

Figure 5.9. Digestion of the snack pastes' protein by digestive enzymes:1 – pepsinolysis, 2 – tripsinolysis

Relevant thermal processing and sodium citrate concentration in the recipe are of great importance for the acceleration of the rate of digestion of the snack pastes' protein. When proteins are heated, they, probably, go through certain denaturation changes, which causes a significant increase of hydrolysis by proteolytic enzymes due to lowering the "structural" barrier [28…31]. At the same time, excessive thermal processing does not lower the snack paste protein's biological value (Table

5.4). The rate of proteolysis of the snack pastes' protein (Figure 5.9) compared to the control sample – fat-free lactic acid curd – grows by 45×60 s with the raise of sodium citrate concentration to 2%.

The fulfilled research of the mineral composition (Table 5.8) has shown that the sol residue of the snack pastes contains macro- and micro-elements. The snack paste is a significant source of calcium, phosphorus, potassium, and sodium. Besides, it is rich in such important mineral substances as iron and manganese.

Table 5.8 – Results of the research of the snack pastes' mineral composition

Name of substance	Content, mg/100g	
	Control	Paste
Calcium	120	117
Phosphorus	189	126
Potassium	117	95
Sodium	44	35
Iron	0,3	0.16
Manganese	0.0078	0.006

The investigations of the vitamin composition of the snack pastes (Table 5.9) has shown that they are rich in soluble vitamin (E) tocopherol and water soluble (P-P) niacin.

Table 5.9 – Results of the research of the snack pastes' vitamin composition

Name of vitamin	Content, mg/100g	
	Control	Paste
Vitamin A (retinol)	0.01	0.004
Vitamin E (tocopherol)	–	15.50
Vitamin B_1 (thiamine)	0.04	0.028
Vitamin B_2 (riboflavin)	0.25	0.172
Vitamin PP (niacin)	0.45	0.228

The investigations of the fatty acid composition of lipids of the snack pastes (Table 5.9) has shown that they contain both saturated and unsaturated fatty acids. There are 14.19% of saturated fatty acids in the total fatty acid content including palmitic acid (8.3%) and stearic acid (4.1).

The total content of unsaturated fatty acids is 86.97% including a high content of unsaturated linoleic acid (61.97%) and monounsaturated oleic acid (23.47%) (Table 5.10).

Table 5.10 – Results of the research of the snack pastes' fatty acid composition

Fatty acid		Content, %		
Name	index	Purified deodorized sunflower oil	freshly-made sample	after 28 day storage
Palmitic	$C_{16:0}$	6.17	8.52	10.43
Palmitoleic	$C_{16:1}$	traces	<0,2	0.22
Stearic	$C_{18:0}$	3.43	4.25	3.78
Arachic	$C_{20:0}$	0.68	0.68	0.46
Saturated		10.52	13.65	16.16
Oleic cis.	$C_{18:1\ cis}$	23.38	23.57	23.06
Oleic trans.	$C_{18:1\ tr}$	0.60	0.57	0.30
Linoleic	$C_{18:2}$	65.25	62.21	60.48
Unsaturated		89.48	86.35	83.84
Total		100	100	100

During the investigation of the fatty acid composition after 28 day storage (Table 5.10) we have noticed an insignificant decrease of the unsaturated fatty acid content (2.4% decrease of linoleic acid, 1.74% decrease of oleic acid). The total content of unsaturated fatty acids decreases by 2.5% due to the increase of the content of saturated and unidentified fatty acids.

We have performed the microbiological and toxicological researches of the snack pastes, the results of which are presented in Table 5.11, 5.12. It has been found (Table 5.11) that c coliform bacteria (colibacillus group) in the finished product stored for 28 days are absent. We have not found any pathogenic microorganisms, salmonellas, staphylococcus aureus, listeria monocitogenes in the investigated samples.

Table 5.11 – Results of the microbiological research of the snack pastes

Indices	Norm	Research results	
		freshly-made sample	after 28 day storage
Colibacilli group (coliform bactria) in 0.1g	no	not found	not found
Staphylococcus aureus, number of conventional units in 0.1g	no	not found	not found
Pathogenic microorganisms, including salmonella in 25g	no	not found	not found
M old, number of conventional units in 0.1g, not more than	1×10^{2}	0.3×10^{2}	0.5×10^{2}
Listeria monocitogenes, in 25g	no	not found	not found

The research has proved that the microbiological indices conform to microbiological and sanitary regulations.

Thus, the snack pastes on the base of fat-free lactic acid curd after the 28 day storage are microbiologically safe for consumption and conform to the regulations.

Table 5.12 – Results of the toxicological research of the snack pastes

Indices	Allowed level, mg/kg, not more than	Real content, mg/kg
Mercury	0.02	<0.010
Arsenic	0.2	<0.10
Copper	4.0	0.80
Led	1.0	0.32
Cadmium	0.2	0.030
Zinc	50.0	11.6

The results of the toxicological research have shown that the snack pastes on the base of fat-free lactic acid curd conform to the safety regulations, microbiological and sanitary norms [37]. Their content of toxic elements is much lower.

Thus, it may be concluded by the results of the changes in the fatty acid composition (Table 5.10) that the snack pastes on the base of fat-free lactic acid curd are safe for consumption and conform to the existing norms.

5.4 Investigating Sensory Attributes of Quality of the Snack Pastes On The Base Of Fat-Free Lactic Acid Curd

To determine the main organoleptic attributes of the snack pastes' quality we have performed the research aimed at developing the qualitative scale of sensory assessment of the finished product on 5-point scale (Table 5.13) [38…41].

Taking into consideration that the developed snack paste on the base of fat-free lactic acid curd is a new product on the modern food market and keeping in mind the threshold deviations in functioning A, B, C, D systems (Figure 5.1), with the help of experts on the base of the sensory assessment scale and taking into consideration the importance coefficients we have performed the sensory analysis [38, 41] of total organoleptic assessment of snack pastes to insure the obtaining of the same quality product (Table 5.14).

Table 5.13 – Development of sensory scale of assessment of snack pastes

Quality level, points	Quality attributes, coefficient of importance				
	Appearance	Color	Aroma	Flavor	Texture
	0.1	0.15	0.28	0.35	0.12
1	2	3	4	5	6
5	Clean, smooth, glossy, uniform surface	Uniform, natural, distinct, characteristic of pastes with relevant name	Natural, clean, distinct, pure, conforms to name, slowly released	Natural, balanced, distinct, pure, conforms to relevant name, slowly released	Plastic, paste-like, solid, structured
4	Smooth, glossy, surface	Uniform, natural, characteristic of pastes with relevant name	Natural, pure, conforms to name, but quickly released	Natural, distinct, pure, conforms to name, but quickly released	Plastic, solid, structured
3	Smooth, slightly glossy, surface	Natural, characteristic of pastes with relevant name	Natural, indistinct, quickly released	Natural, indistinct, conforms to name, quickly released	Solid, not plastic enough, slightly dense or succulent, structured
2	Dull, uneven surface with slight aeration	Natural, intense, characteristic of pastes with relevant name	Indistinct, very quickly released	Indistinct, with alkaline smack, very quickly released	Not plastic, friable, or sticky, fluid, weakly structured
1	Uneven, dull or perforated surface with drops of fat	Natural, nonhomogenous	Sharp, unnatural aroma of aromatizer	With flavor of main ingredients, with distinct alkaline smack	Friable, or gluey, fluid, unstructured

During the sensory research of the freshly-made snack pastes on the base of fat-free lactic acid curd we have established that uniformity and gloss of the

surface, uniform and natural color, paste-like, solid and plastic texture, pure, natural, distinct, quickly released aroma and flavor, as well flavor balance are the most significant characteristics for forming organoleptic attributes.

Each attribute's importance is visually highlighted as a fixed area in the organoleptic assessment profiles (Figure 5.10).

Table 5.14 – Results of the sensory assessment of the snack pastes on the base of fat-free lactic acid curd

Name	# of feature	Characteristic	Mark, points	
			Freshly-made	After 35 day storage
1	2	3	4	5
Appearance	1	Uniformity	5.0	5.0
	2	Non-uniformity	0.9	0.9
	3	Aeration	1.5	0.5
	4	Gloss on the surface	4.0	4.0
	5	Fat drops on the surface	0	0
Color	1	Uniform	4.0	4.0
	2	Natural	4.5	4.0
	3	Intense	1.0	0.8
	4	Distinct	3.5	3.0
	5	Not uniform	1.5	1.5
Aroma	1	Pure	5.0	5.0
	2	Natural	5.0	5.0
	3	Distinct	4.5	4.0
	4	Sharp	0.5	0.5
	5	Rate of release	4.0	3.5
Flavor	1	Pure	5.0	5.0
	2	Natural	50	4.5
	3	Distinct	4.5	4.0
	4	Balanced	5.0	4.5
	5	Rate of release	4.0	3.5
Texture	1	Plastic	4.5	4.0
	2	Paste-like	5.0	5.0
	3	Solid	3.0	4.0
	4	Sticky	0.8	0.8
	5	Succulent	2.0	1.5
	6	Gluey	0.5	0.5
	7	Friable	0.5	0.8

The snack paste on the base of fat-free lactic acid curd with milk fat substituted by purified deodorized sunflower oil is a new product in existing assortment list of traditional paste-like products. It can be used for nutritional

purposes in human's diet both separately and as an ingredient of culinary products [43, 44].

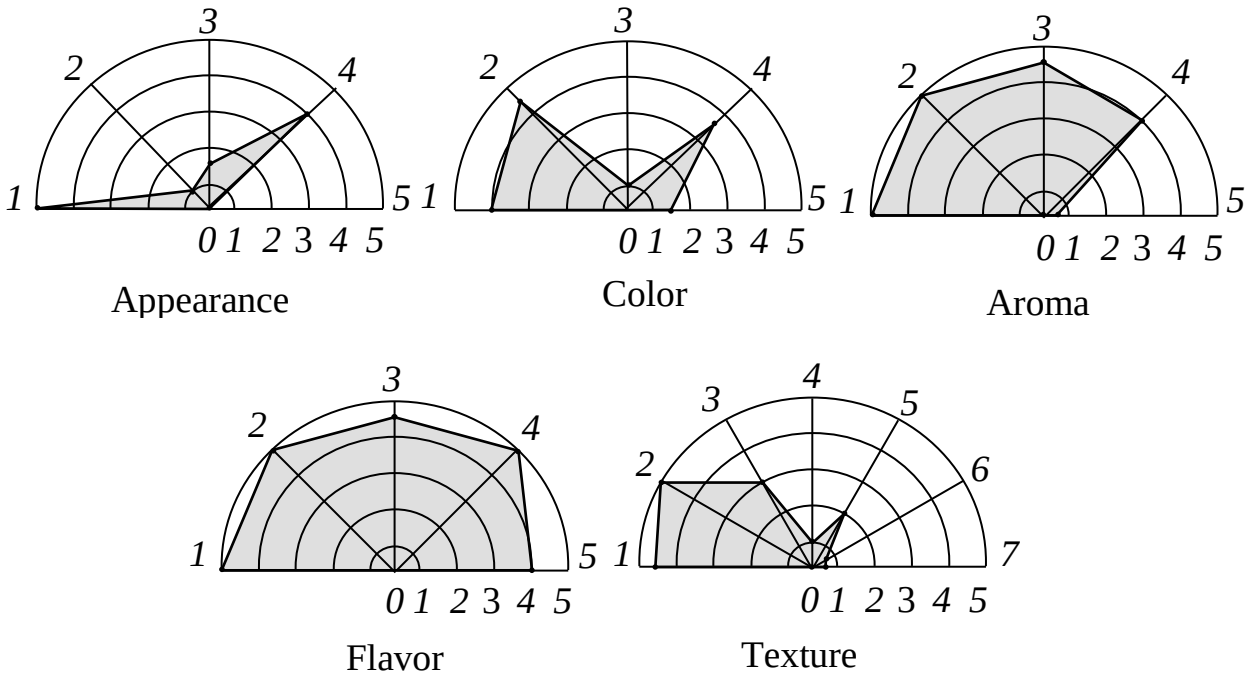

Figure 5.10. Profiles of the organoleptic assessment of the freshly-made snack paste on the base of fat-free lactic acid curd

The investigations of the snack pastes' organoleptic attributes during the 28 day storage in covered polymer material consumer containers at +2…6^{0}C (Figure 5.11) have shown some insignificant changes of texture, decrease of intensity and increase of flavor and aroma release rate.

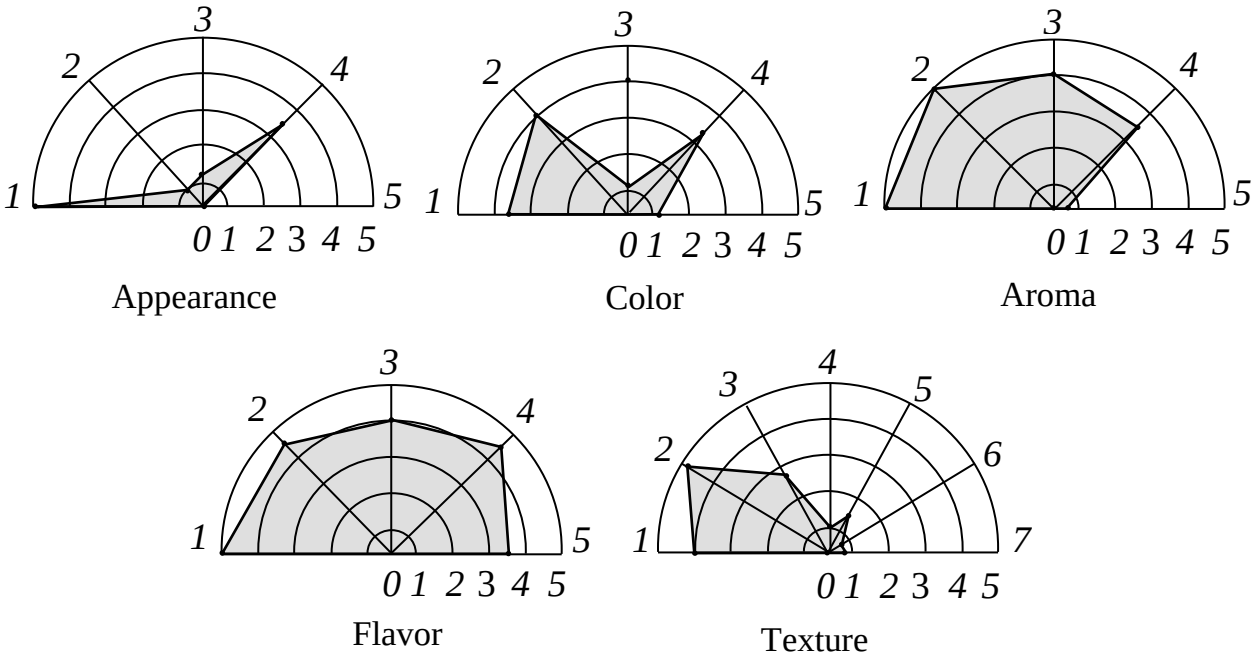

Figure 5.11. Organoleptic profiles of assessment of the snack paste on the base of fat-free lactic acid curd after 28-day storage

To check the adequacy of the influence of optimal concentrations of the main ingredients [45, 47] and water/DDMR (dry defatted milk residue) ratio on quantitative dependence and form of binding of quality coefficient on technological agents to define the complex quality index (Figure 5.12) we have performed the expert assessment of the snack paste samples with lactic acid curd content within 20…50%, vegetable oil content within 20…35%, agar content within 1.1…1.5% and with water/DDMR ratio within 0.8…2.4, and investigated the kinetics K_p depending on lactic acid curd, vegetable oil, and agar contents in the framework of the two-parameter model (K_p is technological parameters).

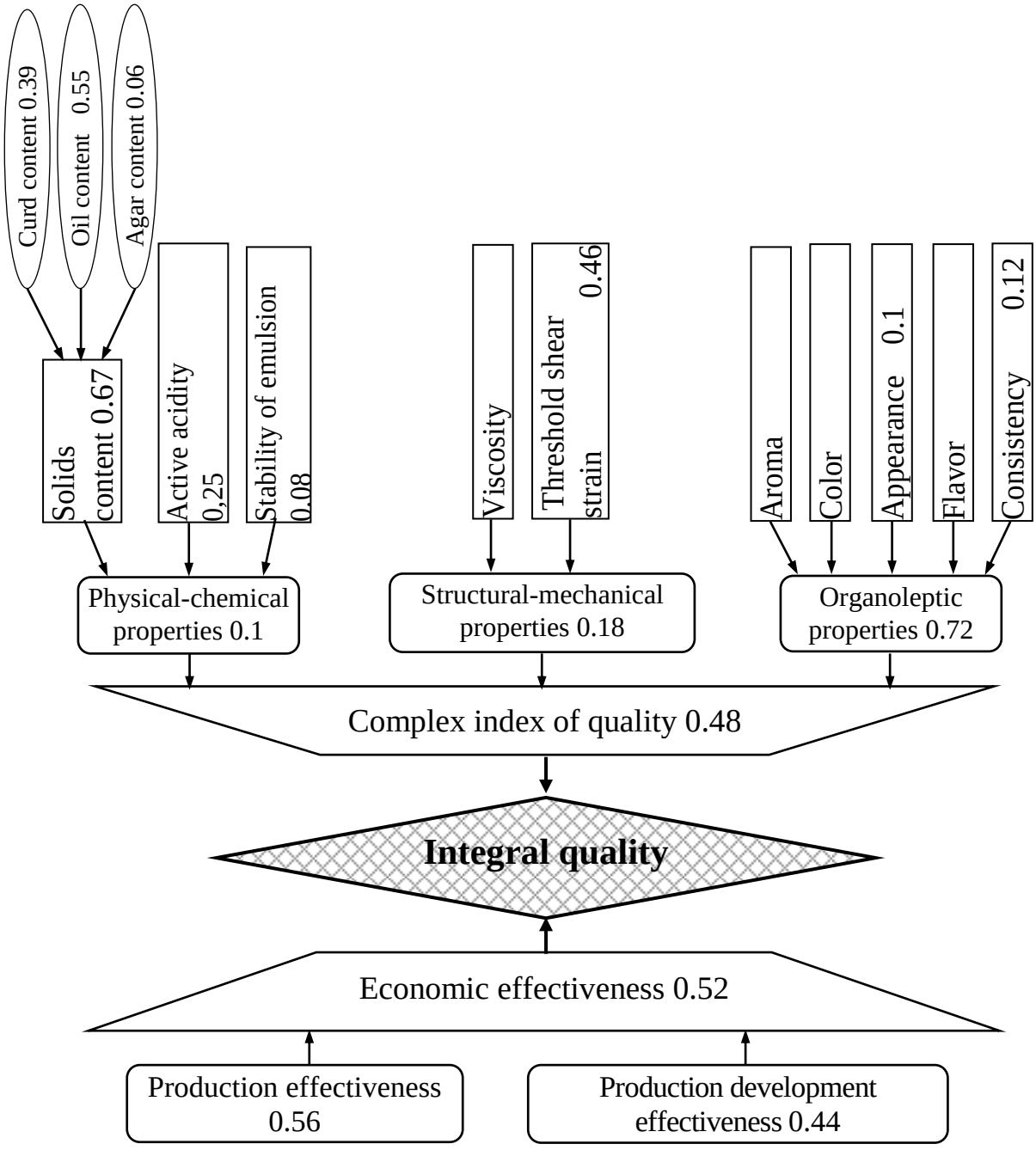

Figure 5.12. Formation of the snack pastes' integral quality index

The technological factors' influence on the snack paste's quality was assessed by modeling the complex quality coefficient of the finished product (K_p), which was derived expert assessment taking into consideration experts' agreement. The concordance coefficient (Kendell) was chosen not less than 0.95. In case of a weak expert agreement the number of experts increased [187, 189]. We believe that K_p has one local extremum within the change of the technological agents (lactic acid curd, vegetable oil, agar).

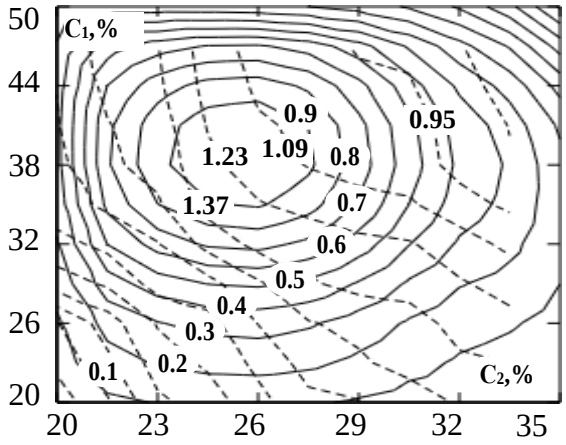

Figure 5.13. Overlap of the lines of equal values of relative quality coefficient K_p at optimal contents of fat-free lactic acid curd (C_1), sunflower oil (C_2) and water/DDMR ratio

The modeling [45, 50, 51] helped establish that the dependence of $K_p(x)$ in the snack pastes' recipe is as follows: for lactic acid curd it is of fractional rational function character (equation 5.1); for vegetable oil it has the character of logarithmic dependence on the fourth order polynomial (equation 5.2); for agar it is of square of order polynomial character (equation 5.3):

$$K_p(x) = \left(\frac{-0.0030 + 0.0067 \cdot x - 0.0001 \cdot x^2}{1 - 0.063 \cdot x + 0.001 \cdot x^2 - 1.216 \cdot 10^{-5} \cdot x^3} \right)^2 \qquad (5.1)$$

To define the optimal values of water/DDMR ratio – one of the main factors of forming the snack paste structure – and fat-free lactic acid curd's effect on it we calculated K_p and built its dependence on fat-free lactic acid curd, vegetable oil, agar content in the framework of two-parameter models and water/DDMR ratio (Figure 5.13, 5.14).

It has been found that the relative quality coefficient's value is maximal when fat-free lactic acid curd content is 40%, and water/DDMR ratio is 1.35 (Figure 5.13), which agrees with the results of modeling of the snack pastes' complex quality index.

The changes of the quality coefficient depending on the vegetable oil content in the snack paste was calculated by equation 5.2.

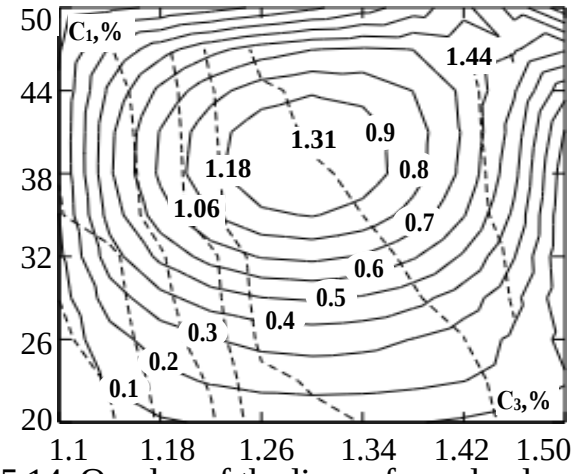

Figure 5.14. Overlap of the lines of equal values of relative quality coefficient K_p at optimal contents of fat-free lactic acid curd (C_1), agar (C_3) and water/DDMR ratio

It has been found that K_p is maximal when vegetable oil's content is 25%, and water/DDMR ratio is 1.26 (Figure 5.13). The obtained result agrees with the expert assessment of vegetable oil's effect on the snack pastes' quality.

$$K_p(x) = \frac{0.092 + 0.039 \cdot \ln x - 0.075 \cdot \ln^2 x + 0.024 \cdot \ln^3 x - 0.002 \ln^4 x}{1 - 0.324 \cdot \ln x - 0.281 \cdot \ln^2 x + 0.148 \cdot \ln^3 x - 0.018 \cdot \ln^4 x} \qquad (5.2)$$

The kinetics of the snack pastes' quality coefficient depending on agar content was defined by equation 5.3:

$$K_p(x) = \sqrt{936.3 - 2974.8 \cdot x + 3505.7 \cdot x^2 - 1815.7 \cdot x^3 + 348.8 \cdot x^4} \qquad (5.3)$$

It has been found that K_p is maximal when agar content is 1.3%, and water/DDMR ratio is 1.29 (Figure 5.14). The obtained result conforms to the expert assessment of agar's effect on the snack pastes' quality.

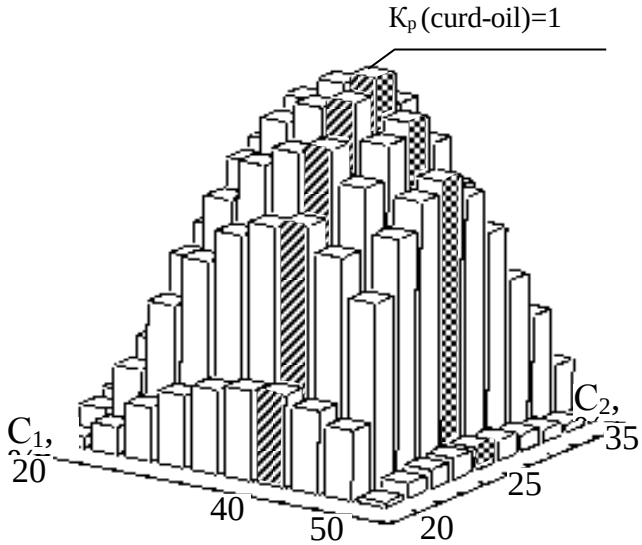

Figure 5.15. Histogram of relative values of quality coefficient of the snack paste K_p on curd (C_1) – oil (C_2) plane

To investigate the dependence of the snack pastes' two-dimensional quality coefficient on the main ingredient's content (Figure 5.15, 5.16) we realized the following algorithm [49, 50,51]:

- possible values of fat-free lactic acid curd and vegetable oil were divided in 10 intervals;
- snack paste samples were made for every possible pair of parameter values (100 samples);
- the assessment expertise of each sample was performed with the set coefficient of agreement ≥0,95;
- the greatest value among the obtained quality coefficients was taken as a scale unit;
- histograms of the dependence of relative values K_p (x) on the main recipe ingredients' concentrations were built on the basis of the obtained experimental data with the help of standard methods of multidimensional statistical analysis.

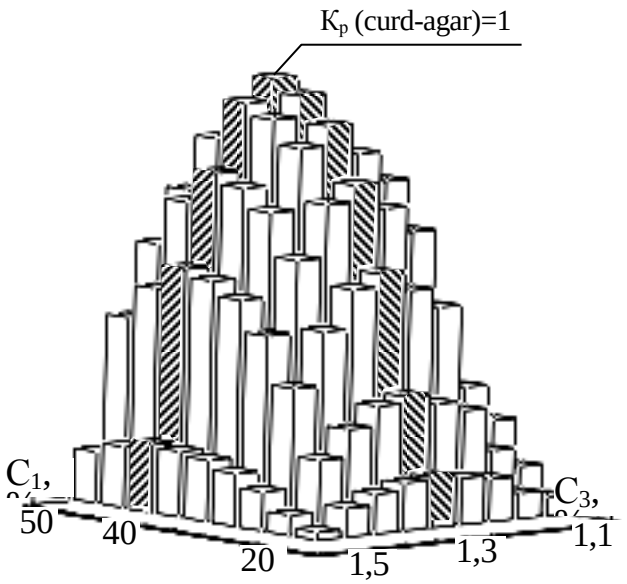

Figure 5.16. Histogram of the relative values of quality coefficient of the snack paste K_p on curd (C_1) – agar (C_3) plane

The histogram analysis has shown that the snack pastes' quality coefficient within the framework of pair models: curd-oil and curd-agar attains maximal values when lactic acid curd content is 40%, purified deodorized oil content is 25%, agar content is 1.3%.

To check the adequacy of the effect of the snack paste main ingredients' content on the relative quality coefficient we modeled its distribution on the basis of the ingredients' optimal concentration values in pair models: fat-free lactic acid curd – vegetable oil (Figure 5.17) and fat-free lactic acid curd – agar (Figure 5.18).

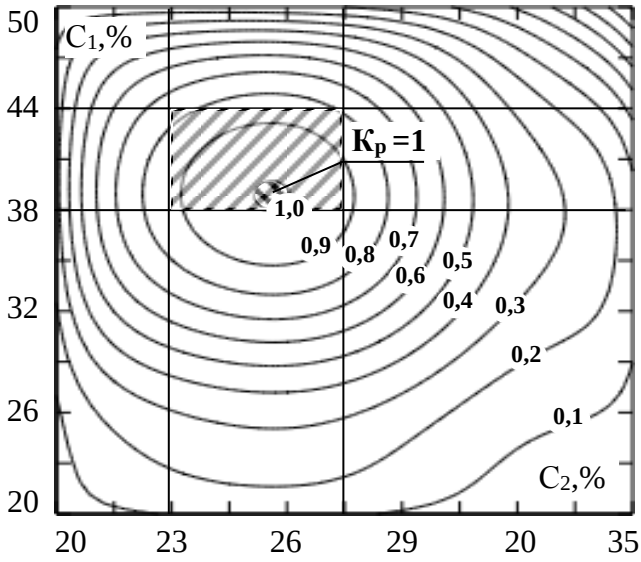

Figure 5.17. Dependence of distribution of the snack paste's relative quality coefficient K_p on optimal content of: fat-free lactic acid curd (C_1), vegetable oil (C_2)

It has been established that K_p is maximal when the curd content is within 39…41% and the oil content is within 25…26%.

The relative quality coefficient in the researched range of the main snack paste components' concentrations is distributed in the following way. K_p is within 1…0.85 when lactic acid content is within 38…44%, it is 0.92…0.97 when oil content is within 24.5…27.5%, which agrees with the expert data.

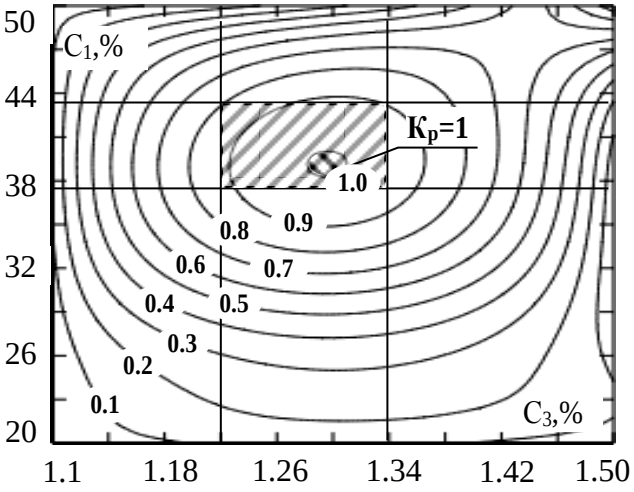

Figure 5.18. Dependence of distribution of the snack paste's relative quality coefficient K_p on optimal content of: fat-free lactic acid curd (C_1), agar (C_3)

The analysis of the fat-free lactic acid curd – agar model (Figure 5.18) has shown that K_p is maximal when curd content is within 39…41% and agar content is within 1.28…1.32%. In the researched range of the snack paste main components' concentrations the quality coefficient is distributed in the following way. K_p is

within 1…0.88 when lactic acid content is within 38…44%, it is 0.88…0.95 when agar content is within 1.22…1.34%, which agrees with the expert data.

To check the adequacy of the combined effect of the thermal processing and the main recipe ingredients'(fat-free lactic acid curd, vegetable oil, and agar) content on the snack pastes' relative quality coefficient we modeled its distribution on the basis of the optimized values of the technological factors and the thermal processing temperature (Figure 5.19, 5.20).

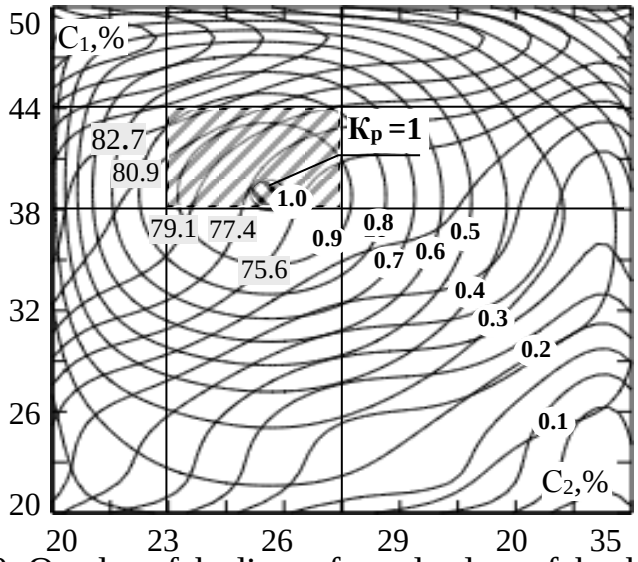

Figure 5.19. Overlap of the lines of equal values of the thermal processing temperature and the relative quality coefficient K_p at optimal contents of fat-free lactic acid curd (C_1), sunflower oil (C_2)

It has been established that when K_p's value is maximal, the temperature of the thermal processing of the snack pastes on the base of fat-free lactic acid curd in the ingredient pair model is 76.8^0C (Figure 5.19).

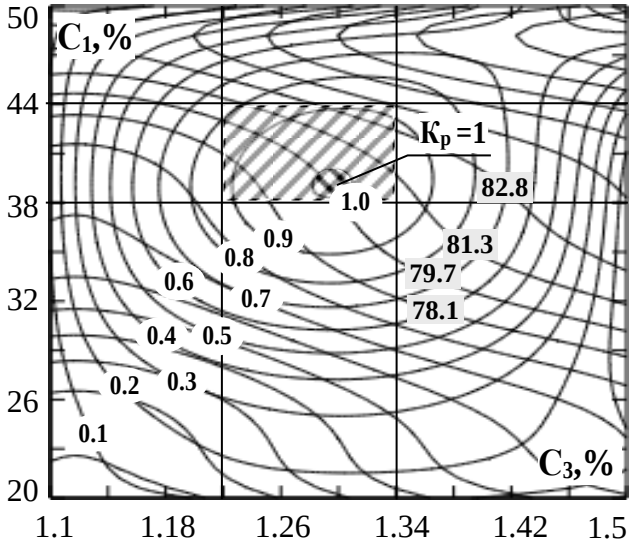

Figure 5.19. Overlap of the lines of equal values of the thermal processing temperature and the relative quality coefficient K_p at optimal contents of fat-free lactic acid curd (C_1) and agar(C_3)

When the lactic acid curd concentration value is optimal 40% and the purified deodorized sunflower oil concentration value is optimal 25%, the thermal processing temperature of the snack pastes is 78.5^0C.

The analysis of the aggregated data on pair model "fat-free lactic acid curd – agar" (Figure 5.20) has shown that when K_p maximal, the temperature of the thermal processing of the snack pastes is 80.2^0C.

When the lactic acid curd concentration value is optimal 40% and the agar concentration value is optimal 1.3%, the thermal processing temperature of the snack pastes is 79.8^0C.

Thus, the optimal content range of the snack pastes' main components provides for the optimal thermal processing temperature range within 80 ± 1^0C, which agrees with the performed experimental researches (Figure 4.26…4.31, 4.35…4.38, 4.40…4.43).

5.5 Developing the Recommendations on the Use of the Snack Pastes as Culinary Products' Ingredients at Restaurants

The performed researches of the nutritional value, structural-mechanical, physical-chemical and qualitative attributes of the snack pastes on the base of fat-free lactic acid curd are the scientific grounds for the development for the recommendations on the use of the snack pastes as culinary products' ingredients [44].

The outcomes of the complex experimental research and the summarization of the processing characteristics led to establishing that the snack paste (ТУ У 15.5-01566330-190:2006) can be used as a separate food product or as ingredient in culinary production (Figure 5.21, 5.22, 5.23).

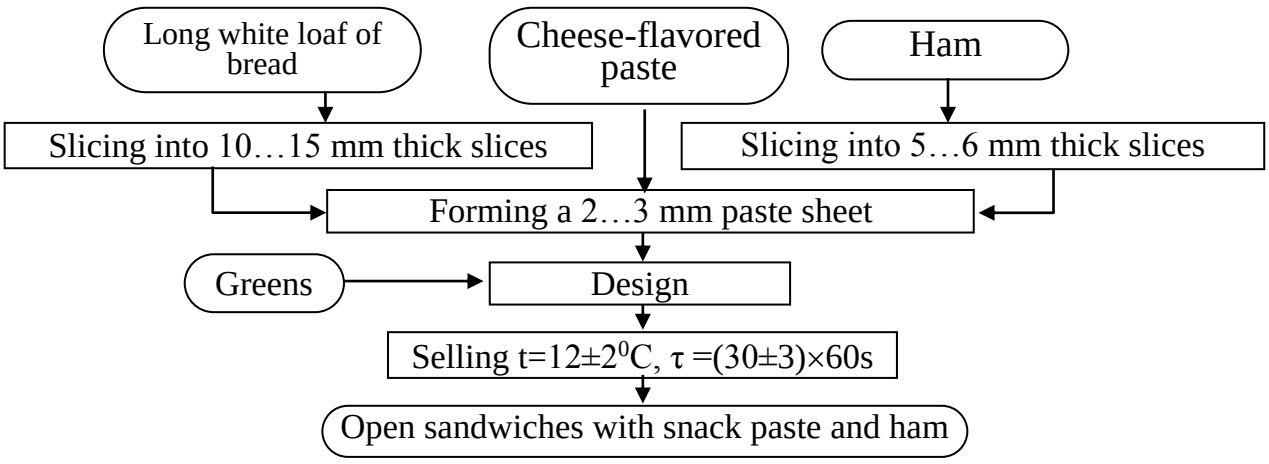

Figure 5.21 Process flowchart of producing open ham sandwiches

During processing investigations and tests, we have developed the recipe composition, processing technology and the assortment of cold snacks: open sandwiches (5 kinds), waffle baskets (5 kinds), salads (5 kinds) and their duly approved processing cards [220].

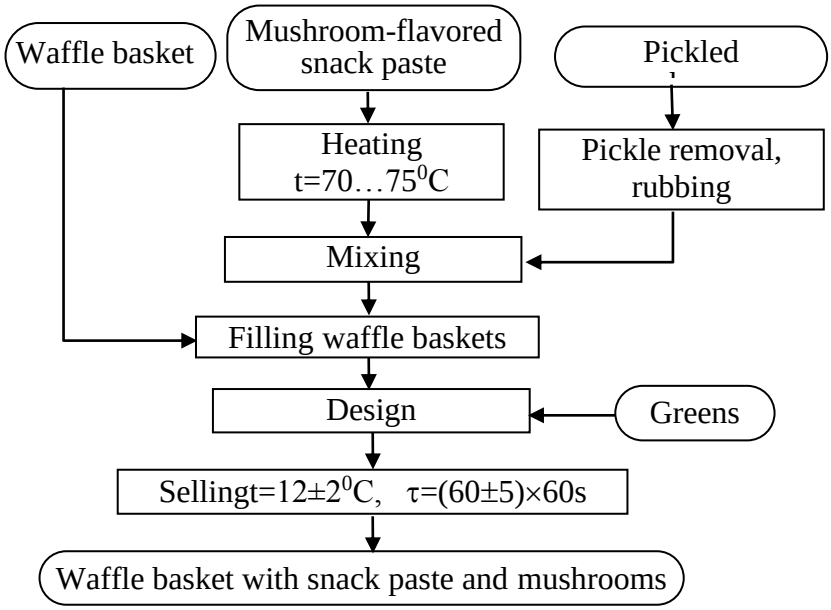

Figure 5.22 Process flowchart of producing mushroom waffle baskets

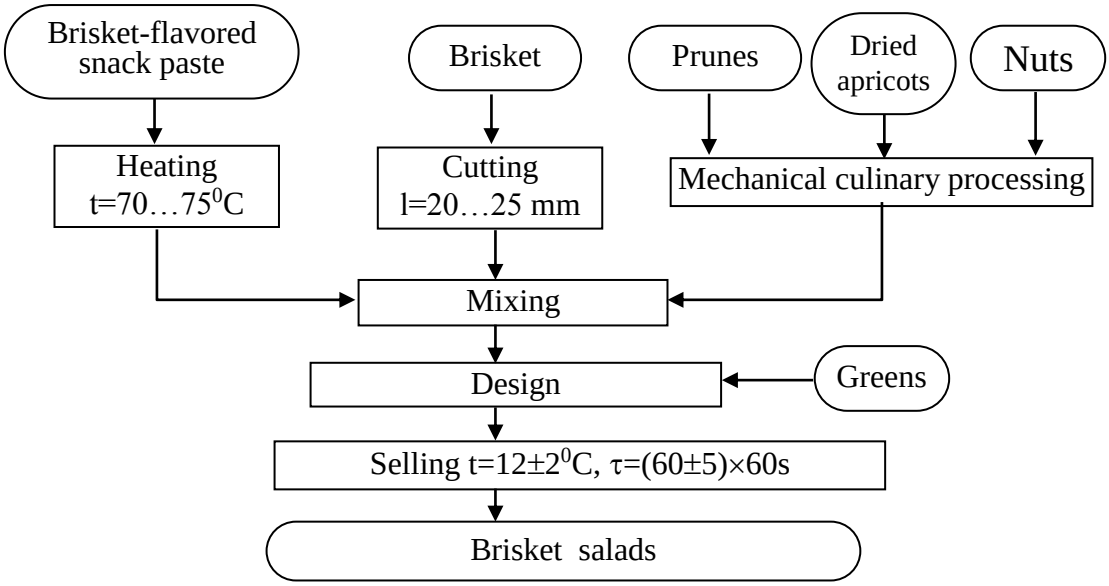

Figure 5.23 Process flowchart of producing brisket salads

On the basis of the performed experimental research it is worth mentioning that the use of the snack pastes in the culinary products' composition allows to offer mass food catering businesses a new assortment of traditional products with

new consumer attributes and raise restaurants' production efficiency owing to the use of multifunctional purpose products.

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