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FOOD TECHNOLOGY USING STRUCTURANTS

The monograph

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The monograph substantiates and develops the technology of gelled products based on gel formers with changed functional properties.

The publication can be useful for a wide range of scientists and practitioners, researchers, graduate students, students majoring in "Food Technology", as well as for practitioners in the food industry and restaurants.

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CONTENT

INTRODUCTION

The main raw materials of confectionery are sugar, molasses, cocoa beans, nuts, fruit and berry semi-finished products, wheat flour, starch, fats, which account for 90% of all raw materials. Additional raw materials that give confectionery piquancy, aesthetic appearance, improve the structure, extend the shelf life are jelly formation agents, food acids and dyes, flavors and emulsifiers, foaming and moisture-retaining additives, etc.

Thickeners and gelling agents are substances that are used in small quantities, increase the viscosity of food, create a jelly-like structure of marmalade products and candies with jelly cases, as well as stabilize the foam structure of pastilles, whipped candy cases. A clear division between thickeners and jelly forming agents is not always possible to find, because there are substances that have the properties of both thickener and jelly forming agent under different conditions. Some thickeners can form strong gels under certain conditions.

The jelly forming agents include: animal gelatin, agar-agar, agaroid, carrageenan, furcelaran, pectin and others. These substances are also hydrocolloids with a long polymer chain, have a high gelling activity that exceeds their thickening activity, and also have different levels of stabilizing activity.

Gelatin (E441) - a protein product that is a mixture of polypeptides with different molecular weights and their aggregates, has no taste or smell. Gelatin is obtained from the cartilage, bones and tendons of animals. Used in the manufacture of jellies and mousses. The advantages of this gelling substance are the transparency of the jellies, elasticity that allows whipping, weak taste. Disadvantages include low gelling ability, slow formation of jellies, reduced gelling ability when boiling. In addition, the hardening of gelatin jellies largely depends on the temperature, so they must be kept for a long time in the refrigerator.

It is known that seaweed synthesizes valuable organic compounds - proteins, polysaccharides, lipids, and are powerful concentrators of many trace elements. Algae industry products (food additives) are used as jelly forming agents, thickeners, gelling agents, adsorbents, antioxidants, emulsifiers, sealants, structurants, fillers. In

some parts of the world, red algae Gigartina stellata (= Mastocarpus stellatus), Chondrus crispus are used to make jelly [1].

Agar (E406) is the strongest jelly forming agent. Is a mixture of polysaccharides of agarose and agaropectin, which is obtained by extraction from red (phyllophora) and brown algae (Gracilaria, Gelidium, Ceramium), growing in the Black, White Seas [2] and the Pacific Ocean. It is a plant substitute for gelatin. Agar-agar is a very universal gelling agent and can be used for food bases with a high concentration of salt, sugar, alcohol, acids. It is used in the confectionery industry in the production of marmalade, jelly, in the manufacture of ice cream, where it prevents the formation of ice crystals, as well as in the clarification of juices. The agar drug is insoluble in water, but when boiled gives weakly concentrated solutions that form transparent jellies when cooled. Jellies of agar have a high melting point, they are dense, transparent, prickly. Their advantages are high gelling ability, transparency, high pour point and melting point. However, this can be a disadvantage in some cases. For example, agar cannot be used to make mousses and sambuca, because in the process of beating it hardens very quickly [3]. Unlike other thickeners such as pectin and gelatin, agar begins to give the gel at a concentration of 0.3-0.5%. The dosage depends on the quality of the agar, the presence of other ingredients in the formulation, which enhance or weaken its effect. The use of agar in food production or other industries is based primarily on its features soluble in hot water and subsequent cooling to create a jelly-like structure. In general, agar-agar is one of the strongest gelling agents, the strength of which is measured in conventional units, the most popular brands 900, 1000 and 1100.

Agaroid (Black Sea agar) in gelling ability is 2 times higher than gelatin, and at a cost 3 times cheaper. In the production of marmalade, the ability of agaroid to jellies formation is about 3 times less than agar and 2-2.5 lower than pectin. It is made from the Black Sea algae filophora nerloza, which has leaves no thicker than 5 mm in the form of porous plates. The color of the product can vary from light gray to ash gray with a permissible yellow tint. Agaroid is poorly soluble in cold water and well in hot. Agaroid swollen in water at a temperature above 75 ℃ dissolves well in water, forming capable of solidifying solutions. This makes it possible to store the

jelly without disturbing the shape at room temperature. An aqueous solution of agaroid (sol) after cooling forms a jellies (gel) at concentrations of 0.8-1%. The jelly-forming properties of the agaroid solution are reduced if the acidified solutions are heated to 60 ℃ and above. The disadvantage of agaroid is the ability to precipitate proteins, therefore it is impossible to prepare milk jelly on an agaroid. For the same reason, an agaroid solution cannot be combined with a gelatin solution. The hydrophilic properties (water retention) of agaroid are weaker than those of agar and pectin, so the jellies of agaroids dry faster and form sugar crystals.

Carrageenans (E407) contained in Eucheuma sp., Chondrus crispus, Gigartina sp., Furcellaria lumbricalis, Hypnea sp. are widely used in the food industry because they have unique stabilizing and sealing properties, they improve the structure of the product, increase the yield of the finished product, add elasticity and resilience, resistance to syneresis.

Furcelaran refers to polysaccharides such as carrageenan. It is obtained from Furcellaria lumbricalis (= F. fastigiata) and Phyllophora brodiaei (= Ph. Truncata), in the Baltic countries, in the Baltic Sea [3]. In terms of gelling ability, furcelaran is 4 times higher than gelatin, is a polysaccharide and is similar in its properties to kappa-carrageenan. Furcelaran solutions are resistant to heat. Using furcelaran at a concentration of 0.2-0.5%, can be prepared jelly, and at a concentration of 0.5-1%, jellies are formed without foreign smell and taste.

Pectin is a natural polysaccharide, one of the main components of plant cell walls. The unique properties of pectin as a food and biological additive have led to its special role in the economies of developed countries. Pectin is widely used in various branches of the food industry as a gelling agent, stabilizer, thickener, emulsifier, and as an effective complexing agent, natural radioprotector,dietary supplement in the production of therapeutic and prophylactic, health products,, medicine and pharmacological industry; pectin is widely used in the manufacture of cosmetics and other sectors of the economy. The world has a steady increase in pectin consumption by 3.0-3.5% annually, so this production is developing rapidly, improving pectin technology from various secondary plant raw materials.

One of the most important directions of increasing the efficiency of modern production is the creation of technologies with a wide involvement of secondary raw materials, which, especially now, is needed by the processing industry of the agro-industrial complex of Ukraine.

In addition, the development of food products, including functional direction, with the addition of jelly forming agents from seaweed, pectin and pectin products - an important factor in reducing a number of diseases.

The monograph contains research materials that include the characteristics and functional properties of structurants and an overview of modern methods of integrated use of structurants of different nature to obtain a wide range of structured foods.

1 GENERAL CHARACTERISTICS OF STRUCTURE-FORMING AGENTS AND THEIR PROPERTIES

1.1 Characteristics of structure-forming agents (agar, agaroid, furzellaran, gelatin) with altered functional properties

1.1.1 Investigation of the moisture absorption kinetics.

The process of producing jelly products in one of the first stages involves the moisture absorption of xerogels in order to receive when heated viscous solutions.

The process of moisture penetration into the inner area of the biopolymers is diffusive and is described by the equation of non-stationary diffusion. A special case of its decision is:

$$e^{-k\tau} = \frac{W_e - W_c}{W_e - W_i}, \qquad (1.1)$$

where Wc – the current value of object moisture;

W_i, W_e – initial and equilibrium moisture content of the object;

k – the rate constant of the moisture penetration process into the inner area of the object, s^{-1};

τ – time, s.

The transfer of moisture from the environment to the inner area of the particle occurs under the influence of the moisture absorption difference at the boundary of the solid and liquid phases. At the initial moment of time, the driving force of the process is maximum, and over time – decreases and at equilibrium moisture absorption is zero.

The maximum amount of moisture that can be absorbed by porous isotropic particles consists of the moisture that fills the vapor space (voids) inside the particles and the moisture absorbed by the high molecular weight compounds of the solid.

The kinetic curves calculated by equation (1.1) and obtained experimentally, presented in table 1.1 and show the dependence of the amount of moisture absorbed on the concentration of sodium salts (lactate and sodium chloride) contained in the environment.

The difference between experimental and theoretical data is negligible, and the standard deviation does not exceed 5%.

The analysis shows that in the presence of food acids salts , the amount of moisture absorbed by the agaroid is reduced compared to swelling in water. So, the first 30… 60 seconds of soaking the xerogel in water, the moisture content was 9.67×10^{-3} kg, in the presence of 0.036 M sodium lactate – 9.44×10^{-3} kg, in the presence of 0.18 M – $7{,}81\times10^{-3}$ kg, 0.18 M of sodium chloride – 7.83×10^{-3} kg, 0.108 M – 4.87×10^{-3} kg.

The most intense swelling process of agaroid particles, occurs both in the presence and without additives, takes place within 40… 60 s when absorbed up to 90% and more total amount of moisture that the particle can absorb.

Table 1.1 – Water absorption kinetics of agaroid in the presence of sodium salts of food acids

Supplements, Moles	**The amount of moisture, 10^{-3} kg, absorbed by the agaroid, calculated experimentally, with swelling for τ × 60, s**									
	10		**20**		**30**		**40**		**60**	
	W^*_E	W^{**}_T	W_E	W_T	W_E	W_T	W_E	W_T	W_E	W_T
Lactate Na										
0.00	5.58	5.74	8.42	8.44	9.67	9.75	10.5	10.4	10.9	10.8
0.036	5.31	5.69	8.30	8.30	9.44	9.52	10.2	10,1	10,5	10,5
0.09	4.83	5.60	7.41	7.96	9.03	9.00	9.69	9.45	9.78	9.77
0.18	4.73	5.04	7.18	7.18	7.18	8.01	8.21	8.52	8.79	8.79
0.36	3.92	4.00	5.54	5.69	6.29	6.43	6.75	6.75	6.99	6.98
Chloride Na										
0.000	5.59	5.41	7.68	7.77	8.95	8.94	9.48	9.50	9.91	9.90
0.018	4.66	4.72	6.72	6.87	7.83	7.87	8.27	8.34	8.68	8.67
0.054	3.67	3.62	5.30	5.29	5.99	6.09	6.33	6.47	6.73	6.75
0.108	3.23	3.10	4.47	4.45	4.87	5.08	5.33	5.37	5.60	5.57
0.162	2.43	2.45	3.66	3.56	4.01	4.09	4.32	4.35	4.59	4.53

W^*_E - amount of moisture absorbed by the agaroid (experimental);
W^{**}_T – amount of moisture calculated theoretically.

The dependence of the rate constant of moisture absorption and the equilibrium moisture content of samples of agaroid on the concentration of salts introduced into the medium for moisture

absorption is presented in Fig.1.1. The graphs show that in the presence of sodium lactate in solution there is an increase in the rate constant of the water absorption process (Fig. 1.1, curve 1). Apparently, anions of organic acid salts contribute to the increase of the diffusion coefficient of moisture in the internal areas of porous isotropic bodies, which are particles of physicolor [4].

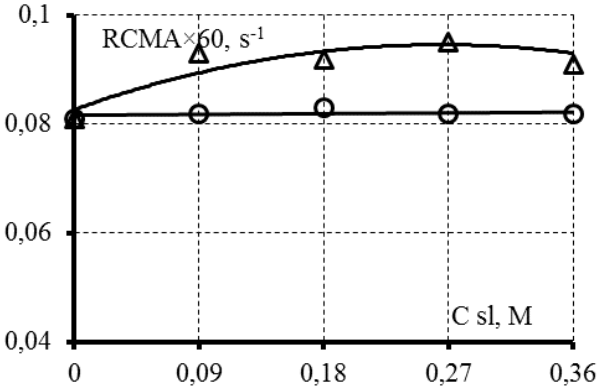


Figure 1.1 – Dependence of the rate constant of moisture absorption (RCMA) by agaroid on the concentration of sodium lactate (1) and sodium chloride (2)

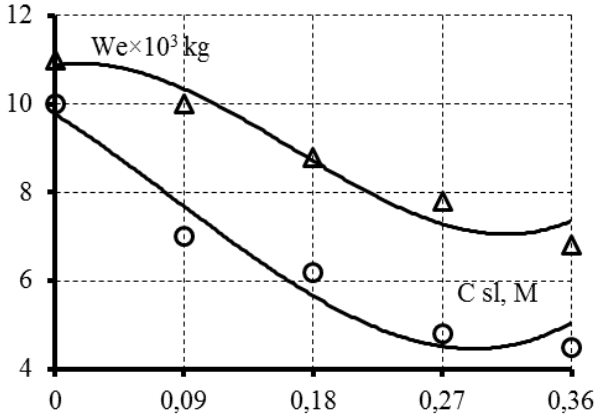


Figure 1.2 – Effect of sodium lactate (1) and sodium chloride (2) on the equilibrium moisture content of the agaroid

The presence of sodium chloride practically does not change the rate constant of moisture absorption (Fig. 1.1, curve 2). But both salts dramatically reduce Wp (Fig. 1.2).

The study of the kinetics of gelatin moisture absorption in the presence of organic acids salts is presented in table 1.2.

Table 1.2 – Kinetics of gelatin moisture absorption in the presence of organic acids sodium salts

The concentration of additives, Moles		Amount of moisture, 10^{-3} kg absorbed by gelatin when swollen for τ×60 ,s					
SL	**SC**	**10**	**20**	**30**	**40**	**50**	**60**
0.00	0.00	2.92	3.78	4.28	4.71	4.81	5.34
0.00	0.01	3.21	3.89	4.45	5.12	5.51	5.42
0.00	0.02	3.17	3.95	4.70	5.28	5.79	5.54
0.00	0.04	3.19	4.08	4.32	5.18	3.26	5.32
0.00	0.06	3.80	3.97	4.18	5.07	2.71	5.01
0.02	0.00	3.00	3.83	4.22	5.09	3.08	5.05
0.05	0.00	2.95	4.00	4.08	5.14	2.72	5.08
0.07	0.00	3.41	4.32	4.47	5.22	5.97	5.81
0.09	0.00	3.40	4.38	4.48	5.03	5.79	5.75

The analysis of the obtained data shows that in the presence of sodium lactate or sodium citrate, the amount of absorbed moisture increases compared to the absorption in water. So, in the first 30… 60 s soaking of the jelly forming agent, the moisture absorption is 4.28×10^{-3} kg, in the presence of 0.01 M sodium citrate 4.45×10^{-3} kg, 0.02 M – 4.7×10^{-3} kg, 0.07 M sodium lactate – 4.47×10^{-3} kg, 0.09 M – 4.32×10^{-3} kg.

The introduced sodium lactate and sodium citrate change the moisture absorption of gelatin depending on their concentration (Table 1.2). From the obtained data it is seen that the increase of moisture absorption of the jelly forming agent occurs at a concentration of 0.01… 0.02 M sodium citrate and 0.07… 0.09 M sodium lactate.

In the presence of alcohol, the rate constant of moisture absorption of the agaroid decreases with increasing its concentration (Fig. 1.3, curve 1), as well as with increasing the concentration of salt and alcohol when introduced together (Fig. 1.3, curve 2). This is because the addition of glycerol increases the viscosity of the liquid phase, and thus complicates the diffusion of such a solution into the internal areas of particles [5]. With the co-introducing of organic acid salts and polyatomic alcohol, the moisture content of the agaroid samples is decreased (Fig. 1.4).

The decrease in the moisture content of the xerogel in the presence of salts and alcohols is probably caused by a decrease in osmosis, and therefore by the diffusion of bound water through the outer shell of the structure-forming particles.

In order to find out the mutual influence of the concentration of organic acids salts (OAS) and polyatomic alcohols on the moisture absorption of gelatin, a study was conducted (Fig. 1.5).

Analysis of the obtained data shows that in the range of concentrations under study, the gelatin absorption does not depend on the amount of alcohol injected. Organic acid salts selectively influence on changes in the moisture absorption amount. Thus, in the presence of sodium citrate at a concentration of 0.01… 0.02 M increases to 5.7×10^{-3} kg, the extremum for sodium lactate is in the range of 0.07… 0.09 M, and the magnitude of the equilibrium moisture content will increase to 6.3×10^{-3}kg. When co-administered with alcohol and salts, the level of moisture absorption increases to 6.3×10^{-3}kg, which corresponds to the swelling of the gelatin in the presence of only sodium lactate.

A significant factor affecting the moisture absorption process is the temperature of the medium.

The amount of moisture absorbed by the agaroid increases with increasing the temperature of the medium (Table 1.4). At the same time, there is also an increase in the intensity of this process.

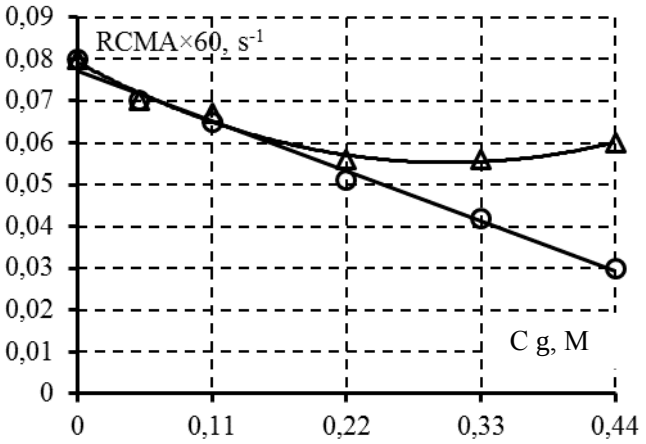


Figure 1.3 – Dependence of the rate constant of moisture absorption by agaroid on the concentration of glycerol (1), sodium lactate together with glycerol (2)

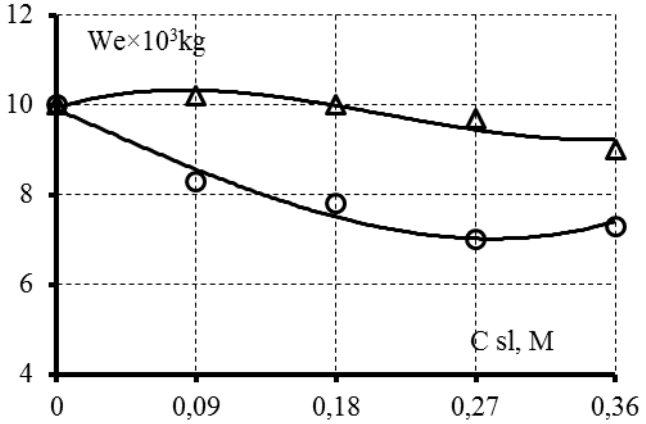


Figure 1.4 – Dependence of equilibrium agaroid moisture content on the concentration of glycerol (1), sodium lactate together with glycerol (2)

Table 1.3 – Kinetics of moisture absorption of agaroid in the presence of sodium lactate and glycerol

The concentration of additives, Moles		Amount of moisture, 10^{-3} kg, absorbed by the agaroid and calculated theoretically, with swelling for τ×60 ,s									
sodium lactate	glycerol	10		20		30		40		60	
		W_E	W_T	W_E	W_T	W_E	W_T	W_E	W_T	W_E	W_T
0.00	0.00	5.59	5.41	7.68	7.77	8.95	8.94	9.48	9.50	9.91	9.99
0.00	0.044	5.26	5.22	7.66	7.74	8.89	9.00	9.68	9.63	10.1	10.0
0.00	0.11	4.78	4.84	7.23	7.33	8.75	8.65	9.40	9.36	10.1	9.9
0.00	0.22	4.49	4.31	6.67	6.70	7.98	8.08	8.79	8.87	9.93	9.8
0.00	0.44	4.00	4.11	6.29	6.37	7.47	7.57	7.92	8.06	8.97	9.1
0.036	0.044	4.25	4.45	6.87	6.67	7.46	7.80	8.36	8.39	9.01	8.9
0.09	0.11	3.86	3.86	5.89	5.86	6.83	6.92	7.61	7.54	8.24	8.1
0.18	0.22	3.37	3.58	5.06	5.23	5.93	6.02	6.56	6.40	6.75	6.6
0.36	0.44	2.21	2.10	3.51	3.55	4.76	4.64	5.52	5.46	6.60	6.5

Table 1.4 – Dependence of the moisture content of agaroid on the temperature of medium

Swelling time, τ, 60	Amount of moisture, 10^{-3} kg, absorbed by the agaroid as it swells in temperature							
	10°C		12°C		15°C		20°C	
	W_E	W_T	W_E	W_T	W_E	W_T	W_E	W_T
10	5.39	5.31	5.58	5.74	6.65	6.73	6.83	7.00
20	7.83	7.77	8.42	8.44	9.38	9.48	9.25	9.50
30	8.85	8.94	9.67	9.75	10.62	10.64	10.38	10.41
40	9.38	9.50	10.50	10.30	11.37	11.12	10.84	10.73
50	9.93	9.70	10.00	10.00	11.40	11.30	10.80	10.80
60	10.00	9.90	10.00	10.00	11.40	11.40	10.90	10.90

Thus, at a temperature of 10 °C the most intense absorption occurs during the first (40… 50) × 60 s, and at a temperature of 15 ° C – within 30 × 60 s (Fig. 1.6).

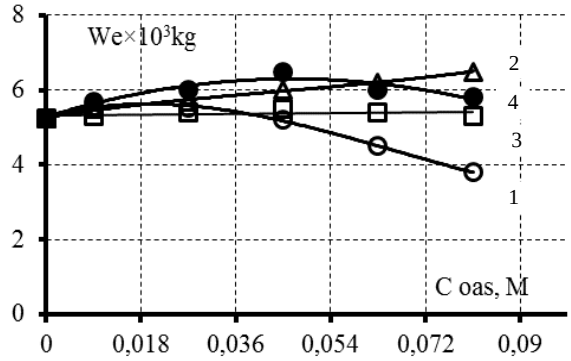


Figure 1.5 – Dependence of the equilibrium moisture content of gelatin on the concentration of sodium citrate (1), sodium lactate (2), glycerol (3), citrate and lactate of sodium together with glycerol (4)

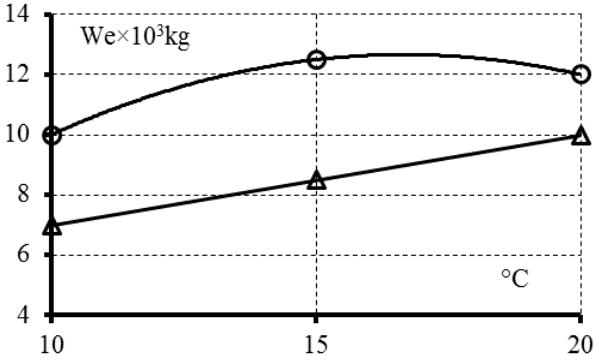


Figure 1.6 – Dependence of speed (1) and degree (2) moisture absorption

Figure 1.6 shows that the increase in temperature is accordingly accompanied by an increase in the rate constant of moisture absorption, that is, the process goes faster, which is probably due to an increase in the intensity of the molecules.

The rate constant of moisture absorption depends on temperature and this dependence is described by the Arrhenius equation:

$$\ln k = B - \frac{E}{R} * \frac{1}{T} \qquad (1.2)$$

where B – a constant that depends on the nature of the biopolymer and the solvent;

E – process activation energy.

The formation of an elastic surface layer on the sample or particles of the sample absorbent polymer causes the phenomenon of osmosis, under the action of which a large amount of solvent accumulates. Therefore, the second stage of moisture absorption leads to a significant increase in volume. Additives of low molecular weight substances to the solvent may affect the flow rate of any of the moisture absorption steps.

The obtained value of the activation energy of the agaroid (21.8 kJ/mole) is approximately twice higher than the energy of thermal motion of the molecules. This indicates that the process of moisture absorption is not just a physical phenomenon of moving the solvent into the pores of the sample due to diffusion, but also a complex colloid-chemical interaction of the two polymer-solvent systems.

A significant decrease of We depending on the concentration of sodium lactate and sodium chloride and a slight change in the rate constant of moisture absorption leads to a osmosis decrease by changing the concentration of the solvent (its decrease) while maintaining its nature. Glycerin also significantly reduces the rate of moisture absorption. However, in the presence of alcohol, the nature of the solvent changes. In addition, the entry of glycerol in the surface layer of the polymer can significantly change the physico-chemical phenomena of the osmotic process in the direction of reducing its intensity.

Summarizing the studies of the moisture absorption kinetics of agaride samples in the presence of various impurities, it should be noted that equation (1.1) was used as a mathematical model of this process, as a special case of the diffusion equation (1.3).

$$\frac{dw}{d\tau} = Dw\left(\frac{d^2w}{dx^2} + \frac{dw}{d\tau} + \frac{d^2w}{dя^2} +\right) + \left(V_x \frac{dw}{dx} + Vy\frac{dw}{dy} + Vz\frac{dw}{dz}\right) \qquad (1.3)$$

where W – moisture content;

dw – diffusion coefficient;

x, y, z – body coordinates;

Vx, Vy, Vz – components of the velocity of the liquid that washes the polymer solids.

The considered modifying ingredients have different effects on the kinetics of moisture absorption, however, the process is described by the selected mathematical model.

The decrease in moisture absorption of sulfated polysaccharides in the presence of salts and polyatomic alcohols can be explained by the deterioration of the solvent from a thermodynamic point of view, the decrease in the repulsion force between macromolecules due to the formation of unstable complexes with low molecular weight additives, reducing the osmotic pressure in the process of moisture absorption, which is associated with a decrease in water concentration.

The process with protein is different. Organic acid salts, like the pH of the solution, affect the electrical balance of the gelatin emphion, altering the macromolecule's configurational state and its affinity for water.

Soaking polysaccharides is advisable to carry out for 60 × 60 s, and gelatin – 40 × 60 s, the optimum temperature of the moisture absorption medium is within 16… 18 ° C, additives are introduced after washing the polymers, or in the last 20 × 60 s of the moisture absorption process.

1.1.2 Study of the surface properties of solutions

The study of the surface properties of solutions and jelly of polymer contributes to understanding the mechanism of possible intermolecular interactions between jelly-forming agents and additives that enhance their jelly-forming ability..

To study the effect of low molecular weight substances on the surface properties of agaroid solutions as a standard solution was chosen with a concentration of agaroid 0.1%. With a larger amount, jelly-formation of the solution introduces a significant error in the measurement of surface tension (б).

Figure 1.7 shows that the agaroid is a surfactant, due to its polar functional groups, significantly reduces the surface tension of the solutions with increasing solution concentration to 0.2% . At a concentration of >0.2%, the structuring of the solution plays a significant role and the surface tension begins to increase. Food acid salts such as sodium lactate and sodium citrate further reduce the surface tension of agaroid solutions.

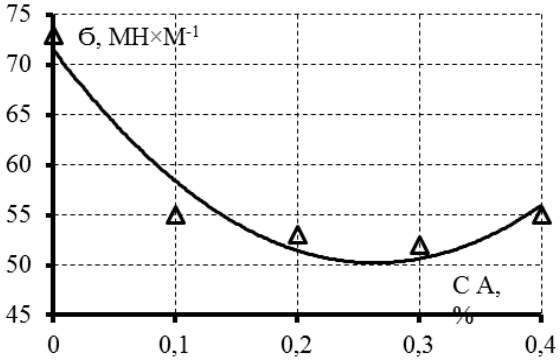


Figure 1.7 - Dependence of surface tension on the concentration of agaroid solutions

Polyhydric alcohols, practically are not a surfactant, in the presence of agaroid and organic acids salts they reduce the surface tension of the solution and the more hydroxyl groups contains in alcohol molecule, the stronger. Moreover, there is no additive decrease in б, which may indicate the emergence of some more surface-active formations between solutes due to molecular forces, due to which low molecular weight additives also affect the structuring of the jelly (Fig. 1.8).

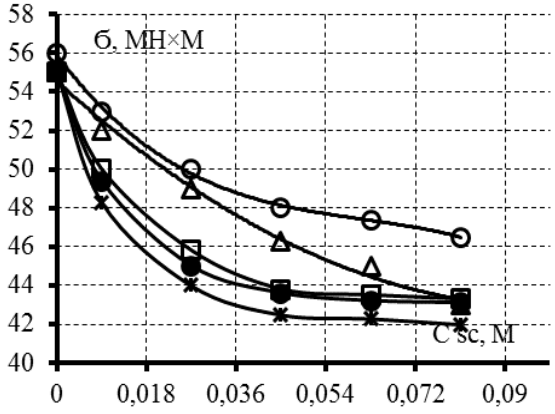


Figure 1.8 - Dependence of surface tension of 0.1% agaroid solutions on the concentration of sodium citrate in the presence of 0.054 M alcohol: 1 - without alcohol; 2 - glycerol; 3 - xylitol; 4 - mannitol; 5 - sorbitol

Addition of sodium chloride (SC) and iron chloride (IC), substances that are not surface-active, leads to an increase in Ϭ of the agaroid solutions (Table 1.5).

Table 1.5 - Changing the surface tension of agaroid solutions in the presence of alcohols and inorganic acids salts

Additives	Surface tension of 0.1% agaroid solutions with the addition of alcohols in concentration			
	0,11 M	0,22 M	0,33 M	0,44 M
Glycerol (Gl)	50.0	50.2	50.6	50.5
Xylitol (Xl)	49.0	49.0	49.2	49.4
Sorbitol (Sl)	48.8	48.8	48.9	49.0
Gl +0,054 M SC	55.1	56.4	57.1	57.8
Xl +0,054 M SC	53.9	54.1	55.1	56.4
Sl +0,054 M SC	52.7	53.0	54.1	55.6
Gl +0,02% SC	54.8	55.5	56.3	56.6
Xl +0,02% SC	53.2	53.7	54.5	55.5
Sl +0,02% SC	52.1	52.6	53.4	54.1

The surface activity of proteins is determined by their spatial structure and the presence of hydrophilic-lipophilic of the molecules areas. Native proteins have a unique, energy-perfectly balanced spatial structure, built on the principle of hierarchy of structures. The amino acid sequence of peptide chains has made it possible to make optimal use of hydrogen bonds, dispersion forces and hydrophobic interactions to stabilize the spatial structure of proteins [6, 7]. Their dyphilic and therefore their surface activity depends on the structure and topography [8]. The isotherm of surface tension of hydrogen solutions of gelatin is shown in Fig. 1.9. The effect of additives on the surface tension was carried out on a 3% solution of gelatin, as this is the main recipe concentration of jelly products.

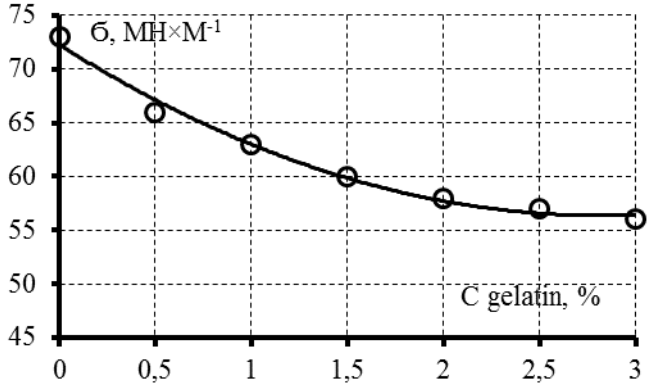


Figure 1.9 - Isotherm of surface tension of gelatin solutions

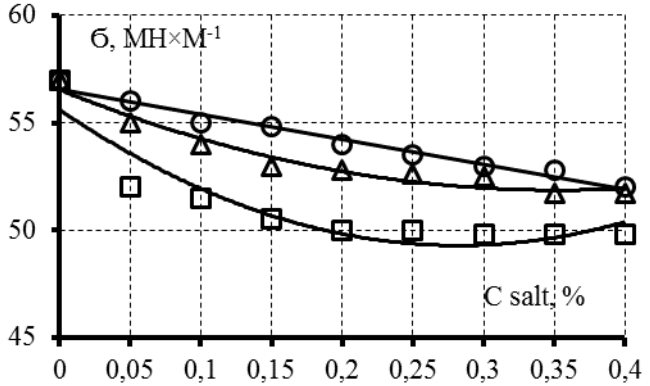


Figure 1.10 - Effect of organic acid salts on surface tension of 3% gelatin solutions: 1- sodium lactate; 2 - sodium acetate; 3 - sodium citrate

The ability of gelatin for molecular interaction with low molecular weight substances was used to improve its functional properties as a jelly-formation. For this purpose, б of gelatin solutions in the presence of organic acid salts and poly atomic alcohols were measured.

The surface tension of gelatin solutions decreases with increasing concentration of organic acid salts (Fig. 1.10). The anions

of salts, in terms of the reducing effect, can be arranged in the sequence:

lactate > acetate > citrate

With increasing alcohol concentration there is also a decrease in the surface tension (Fig. 1.11). And with the increase in the number of hydroxyl groups in the alcohol molecule, the magnitude of the surface tension of the gelatin solution is markedly reduced. Thus, the surface tension of 3% gelatin solutions at a glycerol concentration of 0.2; 0.4 and 0.8 M is 52.5; 61.6 and 50.6 МН×М$^{-1}$ and, accordingly, sorbitol - 51.0; 49.9 and 49.1 МН×М$^{-1}$.

Comparison of surface tension data of gelatin solutions in the presence of organic acid salts and polyhydric alcohols (Table 1.6) shows that the increase of jelly strength is associated with a decrease in the surface tension of the solutions.

Conducted experiments showed that not only cationic surfactants affect the surface properties of solutions of jelly-forming agents, but also anions of organic and inorganic acids, as well as polyatomic alcohols. The effect of their action depends on the hydroxyl groups.

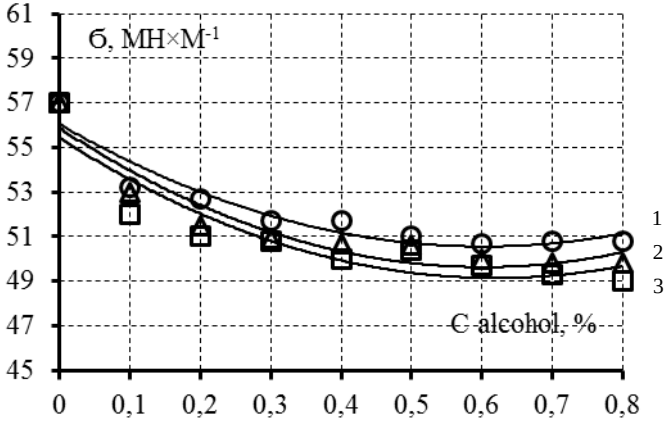


Figure 1.11 - Effect of polyhydric alcohols on the surface tension of 3% gelatin solutions: 1 - glycerol; 2 - xylitol; 3 – sorbitol

Table 1.6 - Changing the surface tension of gelatin solutions in the presence of organic acids salts and polyhydric alcohols

Additives	Surface tension of 3% gelatin solutions with the addition of alcohols in concentration			
	0.11	**0.22**	**0.33**	**0.44**
1	2	3	4	5
Glycerol (Gl)	56.4	56.7	56.9	57.1
Gl +0.08 M SL	56.7	56.9	57.2	57.7
Gl +0.013 M SL	53.9	54.4	54.9	55.6
Sorbitol (Sl)	54.7	54.9	55.7	56.6
Sl +0.8 M SL	56.5	56.6	57.6	58.2
Sl +0.013 M SC	57.7	55.3	53.8	56.7
Gl +0.08% M SL +0.013 M SC	53.3	53.7	54.1	55.3
End of Table 1.6				
1	2	3	4	5
Sl +0.08% M SL +0.013 M SC	53.2	53.7	53.3	55.0

1.1.3 Study of the solutions viscosity

An important technological property of jelly-forming solutions is their viscosity, which determines the behavior of the system at the stage of pouring of jelly products into molds. This property is due to the forces of adhesion between the molecules and represents the resistance of the fluid its movement under the action of external force.

At any rate of deformation, two processes occur simultaneously: destruction and restoration of the structure. The final characteristic that describes the equilibrium state between these processes in a steady stream is viscosity. In Fig. 1.12 shows the changes in the dynamic viscosity of agaroid solutions depending on the concentration of organic acid salts and polyatomic alcohols. Increasing the content of sodium lactate in solution leads to a

decrease in viscosity (Fig. 1.12, curve 1), which is consistent with the data in [8] and is explained by the increase in the charge of macromolecules and the improvement of their solubility. An identical change in the viscosity of the gelatin solution is observed when organic acid salts are added to it (Fig. 1.13, curve 1 and 2). This is due to changes in the shape of the molecules in the gelatin solution as a result of the interaction of organic acid salts with the protein's amino acids. In addition, this process can be caused by a decrease in the electrostatic repulsion forces of the salts. This is confirmed the results ascertaining of the decrease in the viscosity of gelatin solutions with the addition of salts [6], with increasing their concentration in the system, as a result of suppression of electrostatic repulsive forces.

The presence in solutions of polyatomic alcohol (PAA) or alcohol with organic acids salts promotes increasing the viscosity, in the second case - to a greater extent (Fig. 1.12, curve 2.3 and Fig. 1.13, curves 3, 4).

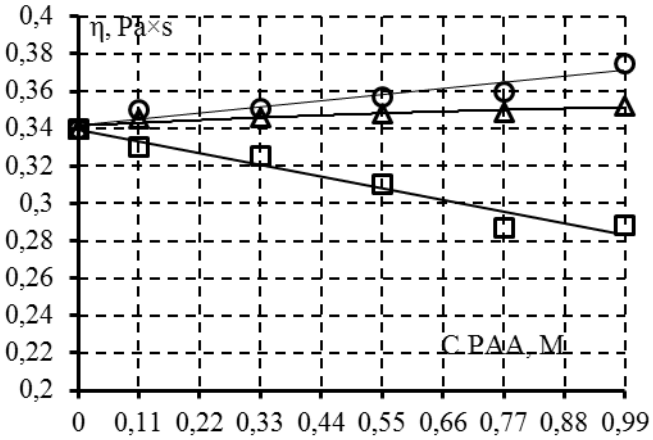


Figure 1.12 - Dependence of viscosity of 4% agaroid solutions on concentration of additives: 1 - sodium lactate; 2 - glycerol; 3 - sodium lactate and glycerol

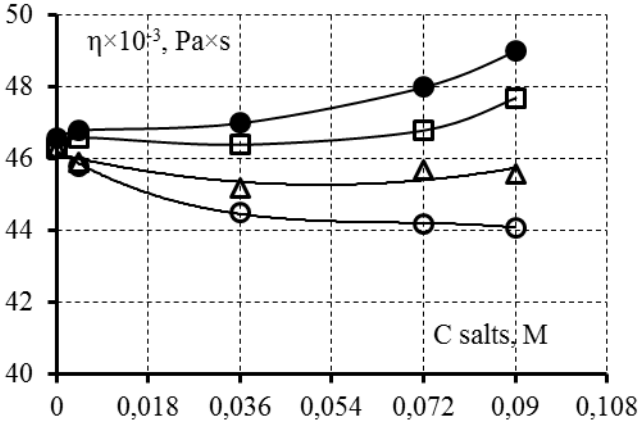


Figure 1.13 - Dependence of viscosity of 3% gelatin solutions on concentration of additives: 1 - sodium lactate; 2 - sodium citrate; 3 - glycerol; 4 - glycerol, sodium lactate and sodium citrate

This trendecy confirms the fact that the introduction of polyatomic alcohols in gelatin solutions can increase the number of hydrogen bonds [7], which are able to form a helical structure of the molecule, which leads to an increase in viscosity compared to the gelatin solution.

1.1.4 Investigation of the supramolecular structure of solutions

In aqueous solutions jelly-forming agents, spirals and bispirals of macromolecules form aggregates or supramolecular parts (SMP). The study of the supramolecular structure of these solutions, the dependence of the size and concentration of the SMP on the conditions of preparation and composition of the solution is important, because the SMP as well as individual macromolecules are fragments of the jelly [8, 9] and determine its physicochemical properties. The energy of the single junction bonds between the SMP and the jelly is about an order of magnitude higher than the energy between the macromolecules, so the strength of the jelly is determined not only by the nature and concentration of the jelly-

forming agents, but also by the concentration of the SMP and their modes.

Modern theory [13] relates structure formation to the interaction not only between free macromolecules, but also to the presence in the solutions of high-molecular compounds of the supramolecular structure, ie particles or blocks formed from macromolecules. Supermolecular particles can interact with each other or with individual molecules. All these types of interactions are participate in the formation of the structure.

The supramolecular structure of solutions of agar, agaroid, gelatin and the effect of additives of polyhydric alcohols and organic acids salts on it have been investigated. It has been found that, regardless of the nature of the jelly-forming agent, an increase in the weight concentration leads to an increase in the concentration of the SMP. The amount of SMP per unit volume increases markedly over time at a given concentration and temperature, and is determined by the technology of solution preparation, its time of its holding, and the rate of cooling of the solution.

Figure 1.14 shows the dependence of the concentration and size of the SMP on the concentration of the jelly-forming agent. The graph shows that for gelatin, unlike agar and agaroid, the concentration of SMP reaches the limit, but the particle size begins to increase. For agar and agaride, the particle size is slightly dependent on the concentration of the jelly-forming agent.

For polysaccharides, as high molecular weight polyanions, it is probably more energy-efficient to production new particles than to grow them. Electrostatic repulsion between macromolecules and supramolecular particles can be a factor that slows down the growth of SMP.

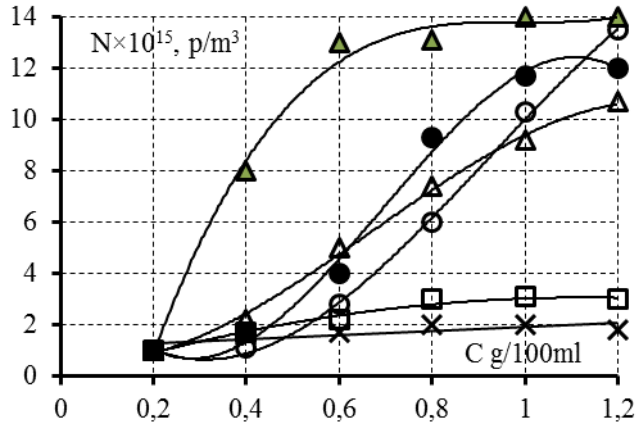


Figure 1.14 - Dependence of concentration of 1- agar ; 2 - agaroid; 3 - the gelatin and the size of the SMP; 4 - agar; 5 - agaroid, 6 - gelatin on the concentration of the jelly-forming agent

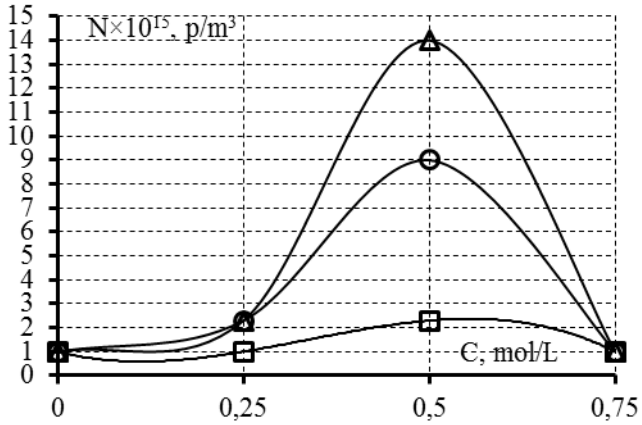


Figure 1.15 - Effect of additive concentration on the concentration of SMP in agar solution 0.2 g / 100 ml: 1 - glycerol; 2 - sodium lactate; 3 - mixtures of glycerol and sodium lactate

Strengthening the bonding between the SMP in the jelly frame compresses the particles over time, reducing their length, that

is, the actual size. This can explain the decrease of particle size over time. The increase in the concentration of agar in the solution leads to the formation of more dehydrated SMP, ie with a smaller effective size.

For gelatin is another. The amphoteric nature of the macromolecule ions creates conditions for the growth of the size and concentration of SMP different from polysaccharides, so the course of the corresponding curves is different..

The influence of the investigated additives of the jelly-forming agent on the concentration and size of the supramolecular particles of the jelly-forming agent depends on its nature, concentration, the nature and concentration of the additive, and has no expressed regularity.

However, at certain concentrations of additives and jelly-forming agent, the size and concentration of SMP can reach the maximum value for these conditions, with the jelly strength noticeably increasing.

As an example in Fig. 1.15 shows the dependence of SMP concentration on the concentration of additives for 0.2 g / 100 ml of agar solution. For agar, the combined effect of polyhydric alcohols and organic acids salts significantly exceeds the effect of each individually and is more than 15×10^{15} m^3.

According to the statement, either polar groups or charged groups or hydrophobic forces take part in the formation of the structure. Based on these ideas explains the results obtained. Alcohols have a mainly dehydrating and solubilizing effect. The strength of the jelly in their presence increases due to the dehydrating effect on the structure formation agent, and the particle size due to solubilization. Assuming that the bond between macromolecules in the SMP is due to hydrophobic forces, then the alcohol molecules, penetrating into the particle, increase in size. The effect is greater than the more hydrophobic alcohol. For polyhydric alcohols, the effect of solubilization is less noticeable due to the steric factor. Organic acid anions can interact with the positive groups of gelatin, thereby binding to the hydrophobic action of the gelatin. The combined action of alcohols and organic acids salts it is creates favorable conditions for the emergence and growth of SMP by reducing the dielectric constant of the aqueous solution and the

degree of dissociation of salts and polar groups of macromolecules. The hydrophobization of gelatin in the presence of the considered additives leads to a certain conformational transformation of macromolecules, which causes the groups to be pushed to the periphery of the SMP.

Thus, for all jelly-forming agents, the combined action of polyhydric alcohols and organic acid salts markedly exceeds the effect of each individually, as well as the additives introduced capable of increasing the size and concentration of supramolecular particles, which is consistent with the strengthening of the jelly structure.

1.1.5 Study of solidification and melting temperatures of jelly

A significant step in the technology of making sweet jelly dishes is the structuring of the jelly system. The parameter characterizing this process and affecting the quality of the finished products is the temperature of the jelly formation of the recipe composition.

In the study of viscosity, it was found that its increase in the presence of additives occurs at temperatures close to the temperature of jelly formation. As modified additives affect the temperature of the formation of the jelly and the melting temperature, it is therefore of practical and scientific interest to study the transition temperature of the solution-jelly in the presence of organic acids salts and polyhydric alcohols.

The formation of the jelly and its melting has a variety of kinetic mechanism. Jelly formation is the sum of the physico-chemical processes that depend on the concentration of the jelly-forming agent and include the rotation of macromolecule particles around specific bonds, the messy group pushes, the ordering, and the stabilization of individual chain and supramolecular particles. The melting of the jelly has all the features of a total transition, which requires the simultaneous rupture of several weak chains, followed by rapid ordering of the chain segments [14].

Polyhydric alcohols and food acids salts have a noticeable effect on the various properties and structure of the structure-forming agents. In the presence of these impurities, the quality of the solvent

deteriorates, affecting the primary intersegmental interaction in the macromolecule of gelatin and the formation of double spirals in the polysaccharide molecules. All this affects the process of formation and melting of jelly.

In the table. 1.7… 1.9 presents experimental data on the change in the solidification temperature (ts) of solutions of agaroid, agar and furcelaran and the melting temperature (tm) of the jelly formed by them in the presence of various additives.

The analysis of the experimental data shows that the temperatures of the jelly formation and melting increase with increasing concentration of additives. Starting with a concentration of 0.044 M alcohol and 0.036 M sodium lactate, temperature values increase linearly and reach maximum values with the co-administration of salts and alcohol.

Table 1.7 - Changing the solidification temperature of the solutions and the melting temperature of the polysaccharide of jelly in the presence of glycerol and salts of organic and inorganic acids

Name of additives	Concentration, M		4% agaroid			2% furcelaran		
	salts	alcohol	t s	t m	t s-t m	t s	t m	t s-t m
1	2	3	4	5	6	7	8	9
Sodium lactate	0.036	0.00	21.0	52.9	31.9	30.5	55.3	24.8
	0.09	0.00	23.0	52.5	29.5	31.5	55.2	23.7
	0.18	0.00	24.5	52.7	28.2	32.5	55.2	22.7
	0.27	0.00	26.5	52.2	25.7	35.0	55.8	20.8
	0.36	0.00	28.5	53.1	24.6	35.5	56.3	20.8
Glycerol	0.00	0.044	21.0	53.5	32.5	27.5	54.1	26.6
	0.00	0.11	21.5	53.9	32.4	28.0	53.9	25.9
	0.00	0.22	22.0	53.4	31.4	28.5	53.6	25.1
	0.00	0.33	22.0	53.8	31.8	29.0	54.2	25.2
	0.00	0.44	23.0	53.6	30.6	29.5	53.5	24.0
Glycerol sodium lactate	0.036	0.044	22.0	52.8	30.8	30.0	56.3	26.3
	0.09	0.11	23.0	52.9	29.9	30.5	55.6	26.0
	0.18	0.22	25.5	53.6	28.1	34.5	56.7	22.2
	0.27	0.33	27.5	54.0	26.5	35.5	57.6	22.1
	0.36	0.44	29.0	54.0	25.5	36.5	57.2	20.7
Glycerol sodium lactate 0,054 M sodium chloride	0.036	0.044	25.0	53.6	28.6	33.0	57.6	24.6
	0.09	0.11	26.5	53.7	27.5	34.5	57.7	23.5
	0.18	0.22	29.0	53.0	24.0	38.0	57.0	19.0
	0.27	0.33	31.5	55.6	24.1	39.0	59.6	20.6
	0.36	0.44	34.0	56.5	22.5	40.0	60.5	20.5
No additives	0.00	0.00	19.5	52.0	32.0	20.0	53.5	33.5

Table 1.8 - Change the solidification temperature of solution and melting temperature of the polysaccharide of jelly in the presence of xylitol and salts of organic and inorganic acids

Name of additives	Concentration, M		4% agaroid			2% furcelaran		
	salts	alcohol	t s	t m	t s-t m	t s	t m	t s-t m
Xylitol	0.00	0.044	21.0	53.6	32.6	28.5	55.6	27.1
	0.00	0.11	21.0	53.9	32.9	29.0	54.3	25.3
	0.00	0.22	21.5	55.2	33.7	30.0	55.0	25.0
	0.00	0.33	22.0	55.2	33.2	30.5	55.6	25.1
	0.00	0.44	22.5	55.8	33.3	30.5	55.3	24.8
Xylitol sodium lactate	0.036	0.044	22.5	54.2	31.7	31.0	55.0	24.0
	0.09	0.11	23.5	54.5	31.0	33.0	55.5	25.5
	0.18	0.22	25.5	55.1	29.6	35.0	55.6	20.7
	0.27	0.33	28.0	55.5	27.5	37.0	56.2	19.2
	0.36	0.44	29.5	56.7	27.2	38.0	56.5	18.5
Xylitol sodium lactate 0,54 M sodium chloride	0.036	0.044	25.0	53.1	28.1	33.5	60.1	26.6
	0.09	0.11	26.5	54.1	27.6	36.0	61.1	25.1
	0.18	0.22	29.0	53.7	24.7	37.5	60.7	23.2
	0.27	0.33	32.0	54.7	22.7	38.5	61.7	23.2
	0.36	0.44	34.0	55.2	21.5	39.8	62.2	22.7

Table 1.9 - Change the solidification temperature of solution and melting temperature of the polysaccharide of jelly in the presence of sorbitol and salts of organic and inorganic acids

Name of additives	Concentration, M		4% agaroid			2% furcelaran		
	salts	alcohol	t s	t m	t s-t m	t s	t m	t s-t m
1	2	3	4	5	6	7	8	9
Sorbitol	0.00	0.044	21.0	53.3	32.3	25.5	55.1	29.6
	0.00	0.11	21.5	53.3	31.8	27.5	55.2	27.7
	0.00	0.22	22.0	53.3	31.3	28.5	56.2	27.7
	0.00	0.33	22.5	53.4	30.9	29.0	56.2	27.2
	0.00	0.44	22.5	53.9	31.4	29.0	56.5	27.5
Sorbitol sodium lactate	0.036	0.044	22.5	53.6	31.1	30.5	56.9	26.4
	0.09	0.11	23.5	53.6	30.1	33.0	58.0	25.0
	0.18	0.22	26.5	54.3	27.8	35.0	57.6	22.6
	0.27	0.33	28.5	55.9	27.4	37.0	57.3	20.3
	0.36	0.44	30.0	55.8	25.8	39.0	58.0	19.0
Sorbitol sodium lactate 0,054 M sodium chloride	0.036	0.044	25.0	54.2	29.2	33.5	61.2	27.7
	0.09	0.11	25.0	54.2	29.2	33.5	61.2	27.7
	0.18	0.22	26.5	54.6	28.1	35.5	61.6	26.1
	0.27	0.33	31.0	55.0	4.0	39.0	62.0	23.0
	0.36	0.44	33.0	55.8	22.8	40.0	62.8	22.8

Thus, the solidification temperature of 4% agaroid (20 ° C) with the addition of glycerol in the amount of 0.11 M (1%) is 21.5 ° C,

in the presence of sodium lactate 0.09 M (1%) - 23 ° C, and the introduction of 0.054 M sodium chloride increases this value to 27 ° C.

It should be noted that depending on the type of additives introduced, the rate of increase of the solidification point of the jelly-forming solutions varies. Thus, in the presence of polyatomic alcohol, the rate of change in temperature averages 0.5 ° C at 0.11 mole/l of alcohol, and in systems "alcohol-sodium lactate" and "alcohol-sodium lactate-sodium chloride" - 2 ° C at 0.11 mole/l alcohol. Thus, the rate of increase of the solidification point of polysaccharides solutions which containing alcohols and salts is 4 times higher than the rate of rise of the solidification point of the samples containing only polyatomic alcohol as an additive.

Addition of sodium lactate significantly alters the melting point of the of the agaroid's jelly. Polyatomic alcohols increase the melting point. However, there was no clear relationship between the number of hydroxyl groups in the alcohol molecule and the change in the rate of temperature rise. The simultaneous addition of organic acid salts and polyatomic alcohol (in the presence of sodium chloride and without it) also increases the melting point of the gels. All of these additives increase the melting point due to their increased concentration.

Analysis of the data in Tables 1.7… 1.9 shows that as the concentration of polyatomic alcohol increases, the melting and solidification temperatures increases and the difference $\Delta t = t_{solid} - t_{mel}$ is decreases. This probably indicates the closeness of the structure of the nodes of the jelly grid at the time of its formation and melting [15].

Glycerol is known to reduce the energy effect of the formation of supramolecular structures. Obviously, the decrease in Δt is explained by the predominance in the systems containing alcohol of double molecular helices as the main nodes of the jelly grid, that is, the predominance in such systems of supramolecular particles as the main nodes of the jelly grid.

Increasing melting and solidification temperatures, as well as increasing the strength of jelly with the addition of organic acids salts and polyatomic alcohols can be attributed to the change in the number [16, 17] of the formed crosslinks, namely, hydrogen.

The formation of the jelly is related to the critical value of the structure formation degree, that is, the hydrogen bonding of the system below which the jelly do not form.

The factors that strengthen of the hydrogen bonding network are the lowering of the temperature, the addition of alcohols and other structure-forming substances [18].

To verify the stated concept, the effect of acetone on the solidification temperature of the agaroid was investigated. Acetone has been selected as a well-studied agent that enhances the bond strength of hydrogen bonds [19].

The measurement results are presented in Fig. 3.16. In the studied concentration range, the solidification temperature increases linearly with increasing acetone concentration. The rate of increase in temperature is 2 ° C per one mole percent of acetone.

The results confirm that the essential role in the mechanism of jelly formation of systems containing organic acid salts and poly atomic alcohols belongs to the hydrogen bond grid. The strengthening of the jelly is due to a large extent to the increase of its hydrogen bond, ie the number of hydrogen bonds in the presence of polyatomic alcohols.

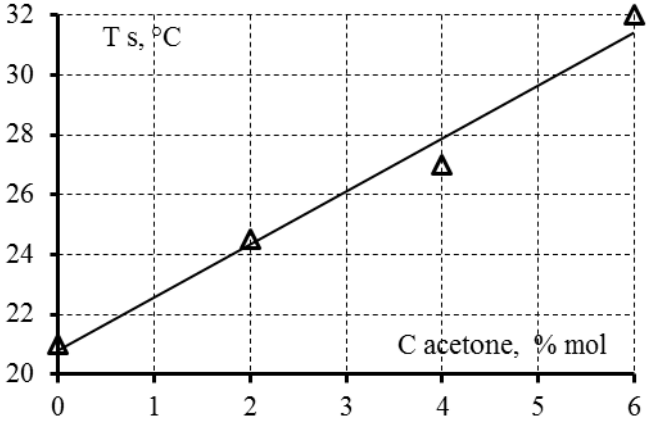


Figure 1.16 - Dependence of solidification temperature of 4% agaroid solution on acetone concentration

The effect of polyatomic alcohols in the presence of Fe (III) ions in the amount of 0.02% on the melting temperature of the jelly of the agaroid was also studied (Table 1.10).

Table 1.10 – The dependence of the melting temperature of the jelly of agaroid on the concentration of polyatomic alcohols in the presence of 0.02% Fe (III)

Additives	Melting temperature, ° C, 4% jelly of agaroid containing 0.02% Fe (III), with the addition of polyatomic alcohol concentration				
	0.044 M	0.11 M	0.22 M	0.33 M	0.44 M
Glycerol	52.8	52.9	53.3	54.8	55.4
Xylitol	53.2	55.3	55.8	56.4	56.3
Sorbitol	56.5	56.3	56.3	56.7	56.7

The results obtained suggest that, in the presence of Fe (III) ions in agar+alcohol systems, the melting temperature is significantly higher compared to these values of the jelly samples containing only alcohol, and also in comparison with the jelly of the agaroid without additives.

It should be assumed that increasing the melting temperature of the jelly with the addition of polyatomic alcohols and Fe (III) ions

is associated with both an increase in the amount of hydrogen bonds as a result of the introduction of alcohols capable of binding water, and the emergence of new bonds in the jelly grid when adding iron ions (III) [20, 21].

Recently, the results of studying the dependence of the jelly melting temperature of different high molecular weight on their concentration have been used to establish the nature of the bonds involved in the formation of the jelly structure [22, 23]. These studies make it possible to obtain information about the state of molecular and supramolecular structure of the jelly formation agent in solution and mechanism of intermolecular interaction.

In the table. 1.11… 1.13 shows the experimental data on the dependence of the solidification temperature of the solution and the melting temperature of the agar, furcellaran and agaroid in the presence of additives Na - Carboxymethyl cellulose (CMC) and $FeCl_3$ on the concentration of the structure.

Table 1.11 – **Changes in the solidification temperature of the solutions and the melting temperature of the jelly of agar from the concentration in the presence of additives Na – CMC and $FeCl_3$**

Agar concentration, C, %	The name of the additive							
	without additives		Na – CMC		$FeCl_3$		Na – CMC + $FeCl_3$	
	t s	t m	t s	t m	t s	t m	t s	t m
0.25	20	60	16	64	26	67	23	68
0.50	28	70	25	72	32	73	30	74
0.75	31	73	28	74	35	75	34	77
1.00	33	76	30	77	37	78	36	79
1.50	38	80	35	81	43	82	42	83
2.00	42	82	40	83	46	84	45	85
2.50	47	84	45	85	50	86	49	87
3.00	52	86	50	87	54	88	53	88
3.50	56	88	55	88	58	89	57	89
4.00	60	89	60	89	61	90	61	90

Table 1.12 – **Changes in the solidification temperature of the solutions and the melting temperature of the jelly of furcellaran from the concentration in the presence of additives Na – CMC and $FeCl_3$**

Furcellaran concentration, C, %	The name of the additive							
	without additives		Na – CMC		$FeCl_3$		Na – CMC + $FeCl_3$	
	t s	t m	t s	t m	t s	t m	t s	t m
0.50	10	30	8	35	15	39	13	42
0.75	13	42	11	48	17	51	15	53
1.00	15	50	13	53	20	55	17	56
1.25	17	53	15	55	22	57	20	58
1.50	19	55	17	57	24	59	22	60
2.00	22	58	20	60	27	62	24	63
2.50	25	61	23	62	29	64	27	65
3.00	28	63	26	64	32	66	30	67
3.50	31	65	29	66	34	67	33	69
4.00	34	67	32	68	37	68	35	70
4.50	36	69	34	69	39	70	38	71
5.00	38	70	36	70	43	71	40	72

Table 1.13 – **Changes in the solidification temperature of the solutions and the melting temperature of the jelly of agaroid from the concentration in the presence of additives Na – CMC and $FeCl_3$**

Agaroid concentration, C, %	The name of the additive							
	without additives		Na – CMC		$FeCl_3$		Na – CMC + $FeCl_3$	
	t s	t m	t s	t m	t s	t m	t s	t m
1	2	3	4	5	6	7	8	9
1.00	8	22	6	26	14	32	12	35
1.25	10	31	8	34	15	40	13	43
1.50	12	38	10	40	16	43	14	44
2.00	15	42	13	43	18	45	15	47
2.50	17	44	15	46	20	47	18	49
3.00	19	46	18	48	22	49	20	51

Continuation of Table1.13

1	2	3	4	5	6	7	8	9
3.50	21	48	19	49	23	51	22	52
4.00	22	50	21	51	24	52	23	53
4.50	23	52	22	52	26	53	25	54
5.00	24	53	23	53	28	54	27	55
5.50	25	54	24	54	29	55	28	56
6.00	26	55	25	55	30	56	29	57

The effect of introduced additives on the solidification and melting temperatures is similar to their effect on the strength of the jelly. Thus, when the Na - CMC polysaccharides are introduced into the solutions, the solidification point is reduced and the melting point is increased compared to the control sample. It also increases the value of the average energy of a single communication node ΔH, which indicates the formation of a stronger structural jelly grid. The introduction of chlorine iron in polysaccharide solutions significantly increases the solidification temperature of the solutions and melting temperatures of the gels. Moreover, a greater effect can be observed for polysaccharides with less jelly-forming ability. The introduced additive reduces the concentration at which a critical break point is observed, characterizing the transition of the molecular structure to supramolecular. Therefore, the transition from the molecular structure to the supramolecular occurs at lower concentrations of the jelly formation agent . Along with the decrease in the critical concentration of the molecular structure transition of the jelly to supramolecular, with the addition of chlorine iron, the average energy of a single communication node Δ H increases (Table 1.14), which indicates the formation of stronger bonds between the molecules of the jelly formation agent. The value of ΔH at introduction of chloric iron grows more than with the introduction of Na - CMC.

Table 1.14 – Critical concentrations and the average energies of a single communication node of jelly of agar, Furcellaran and agaroid

Name of the jelly forming agent and additive	Critical concentration, $C_к$, %	The average energies of a single communication node Δ H, kJ/mol	
		Δ H_1	Δ H_2
Agar	0.50	67.8	113.0
Agar + Na – CMC	0.40	75.1	125.1
Agar + $FeCl_3$	0.30	84.1	128.2
Agar + Na – CMC + $FeCl_3$	0.25	-	129.5
Furcellaran	1.00	28.8	73.2
Furcellaran + Na – CMC	0.90	29.3	88.0
Furcellaran + $FeCl_3$	0.80	30.1	89.2
Furcellaran + Na – CMC + $FeCl_3$	0,75	31.2	94.9
Agaroid	1.50	19.2	69.5
Agaroid + Na – CMC	1.40	19.7	76.4
Agaroid + $FeCl_3$	1.30	22.0	85.4
Agaroid + Na – CMC + $FeCl_3$	1.25	22.6	92.3

Co-introduction of Na - CMC and $FeCl_3$ into polysaccharide solutions occurs increase in the solidification temperature of the solution and melting temperature of the jelly(Table 1.11… 1.13), increase in the average energies of a single communication node of jelly grid, decrease in the critical concentration of the transitionof molecular structure of the jelly in supramolecular structure.

The results of changing the solidification temperature of the jelly of gelatin solutions in the presence of organic acids salts and polyhydric alcohols are presented in Fig. 1.17.

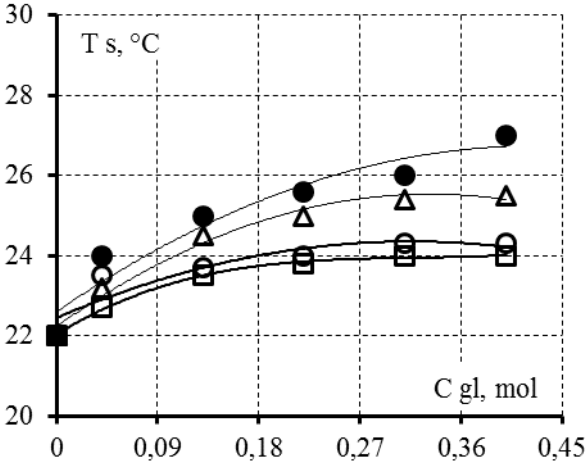


Figure 1.17 - Dependence the solidification temperature of 3% gelatin solutions in the presence of additives: 1- sodium lactate; 2 - sodium citrate; 3 - glycerol; 4 - glycerol, lactate and sodium citrate

The graph shows that the solidification temperature increases with the concentration of additives. Starting the concentration of 0.18 M alcohol and 0.2 M sodium lactate or sodium citrate, the temperature values increase. The maximum value of the solidification temperature is reached with the joint introduction of alcohol and salts. Thus, the solidification temperature of 3% gelatin solution is 22 ° C, at 0.044 M of glycerol is 23.2 ° C, in the presence of salts and alcohol, in the area of this concentration is 24 ° C.

Addition of sodium citrate and sodium lactate does not significantly alter the melting temperature of the gel of gelatin . The presence of polyhydric alcohol, and especially of alcohol together with the indicated sodium salts, contributes to the increase of the melting temperature of the jelly (Fig. 1.18).

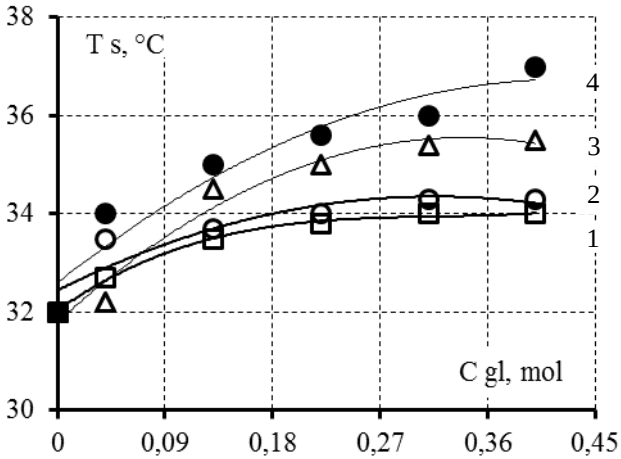


Figure 1.18 - Dependence the melting temperature of 3% gelatin solutions in the presence of additives: 1- sodium lactate; 2 - sodium citrate; 3 - glycerol; 4 - glycerol, lactate and sodium citrate

Thus, the higher the concentration of the listed additives, the higher the melting temperature. Thus, the melting temperature of the jelly of gelatin increases in the presence of sodium citrate and sodium lactate, as well as glycerol, at the most rational concentrations from 32.5 ° C to 34.5 ° C.

It can be assumed that the increase in the melting temperature at a constant concentration of gelatin may be due either to an increase in the average energies of a single communication node, that is associated with an increase in the relative number of bonds which involved in each series of interacting chain segments, or with an increase in the number nodes of the grid.

The conducted complex of researches allows to state that all studied additives increase the solidification point of solutions and melting of jelly. For example, the additives Na - CMC and FeCl3 have been shown to increase the average energy of a single communication node of a jelly grid and reduce the critical concentration of the transition of the molecular structure of the jelly into the supramolecular.

1.2 Characteristics of pectin substances and their properties

1.2.1 Pectin substances of plant

Pectic substances are present in all higher plants; they are the part of cell walls, median plates, cytoplasm of plant cells. Due to their specific properties they perform a number of important functions (regulation of tissue water regime, transportation of water flow, etc.), and participate in the process of cell walls growth. Pectins are found in some alga and sea grass. The amount of pectic substances and their chemical composition are diverse in different plants, their components, tissues, and depend on weather conditions of growth, geographical zones, sort, development period, and age of a plant [4-8].

That is why pectic polysaccharides are considered as one of the most complicated by the structure class of biopolymers [13, 14, 15, 44].

Pectic substances (pectins) are the part of a large group of glycogalacturonans, acidic plant polysaccharides, the main carbon chain of which compose 1, 4 – bond remains of α- D- galacturonic acid [18, 21]. Pectic substances include protopectin, pectic polysaccharides and accompanying arabinans, galactans and arabinogalactans [22, 23].

Protopectin is an insoluble high-molecular pectic complex, which forms cell wall frame and when processed by diluted acids, gives soluble pectin extracted from the plant. There is very little information about the structure of protopectin [24].

Both components of insoluble protopectin and soluble bio polymeric components of plants' juices are pectic polysaccharides.

Aggregate arabinans, galactans and arabinogalactans have composite ramified structure.

Pectic substances are accumulated in a fruit in the process of growth and ripening. This process slows down due to simultaneous accumulation of sugars and other substances. Hereafter pectin partially disassimilates during fruits' storage [30, 31].

Protopectin changing its form to soluble during the fruit ripening predominates in the initial phase of growth. The time and peculiarities of this transition are different for certain sorts depending on the period of ripening, storage abilities and structure of

a fruit flesh. It is known that pectic substances of plants located in a cell wall are tightly connected with cellulose and proteins (by means of arabinans and galactans) [36, 70].

D- galacturonic acid formed in the assimilating plant organs, with C-1 conformation, is the main outgoing substance for pectin biosynthesis in a plant cell. Unramified polymeric blocks are the basis for pectin molecule and are the criteria of biopolymer relation to the category of pectic substances. Golgi apparatus is considered to be the place of polysaccharide fragments' biosynthesis in a plant cell. From here the transition to casings for the formation and polymerization of particular components starts.

Due to the diversity and heterogeneity of pectic substances it is possible to suppose that biosynthesis goes vaguely. The peculiarities of pectic substances transformation in their ontogenesis and their differences depending on the phase of growth and organ where pectin is accumulated (a leaf, scape, fruit, root) [39, 40]. The changes in total pectin content and proportion of soluble pectin and protopectin characteristic for each culture occur in the ontogenesis of plants. Thus, in most fruits the amount of soluble pectin increases while ripening. In beetroot protopectin accumulates in ripening roots. These data demonstrate that role of pectic substances is diverse in vital functions of plants [88].

Soluble pectin and protopectin are located in different parts of a plant cell and perform various functions. Cell wall includes protopectin, from which medial plates are formed; soluble pectin is located in vacuole juice and intercellular layers of ripen fruits tissue [9, 10, 11].

Pectic polysaccharides of a plant cell wall are referred to the class of the most complicated polymers. This complicated construction and its role among the polymers of a cell wall has not yet been clarified [25, 26, 41]. Various methods of research and characteristics of pectic polysaccharides were used for many years. A lot of methods used at present time are based on measuring and interpretation of properties and characteristic of monosaccharide composition. These methods prove potential capability of understanding both structural and functional peculiarities of pectic macromolecules heterogeneity [47]. That is why investigations of individual polymers structure and analysis of their heterogeneity

level within a certain sample are very important for understanding biological macromolecules [31, 37].

Pectic substances are the main component of nutritive plant tissues. Plant tissues are the complex of substances consisting of polysaccharides (cellulose, hemicellulose, pectin), and lignin and protein substances forming cell walls of plants (Fig. 1.1) [27, 28, 37, 73].

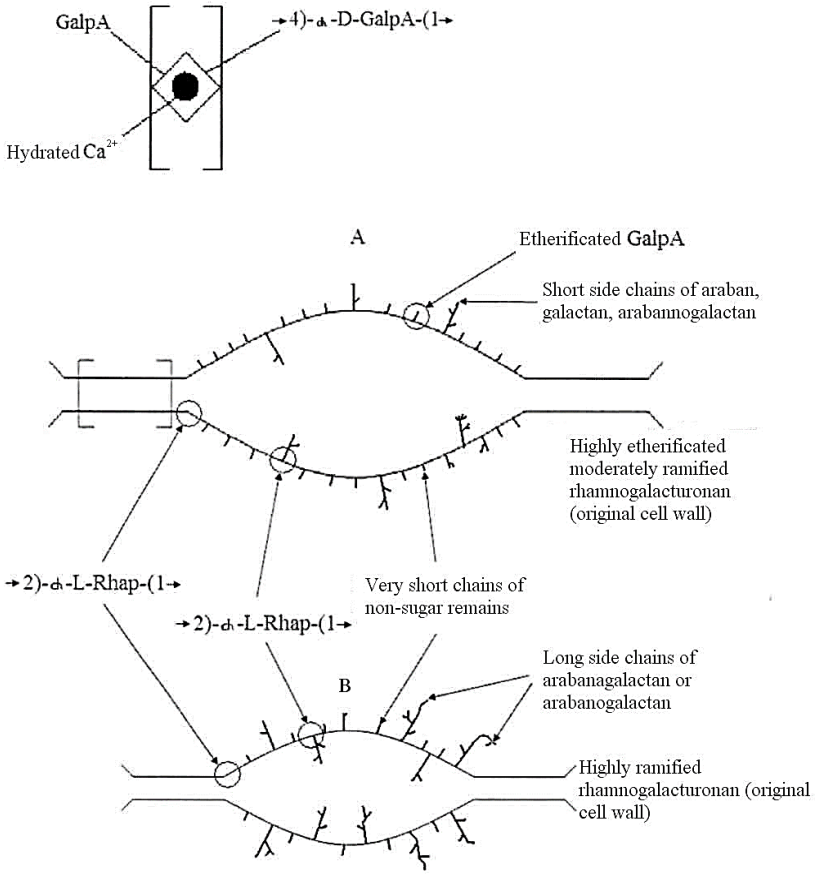


Figure 1.1 – Structural peculiarities of pectic substances of medial plate (A) and original cell wall (B) [72]

Overall scheme of pectic polysaccharides construction includes linear and ramified zones [29, 33, 34] (Fig. 1.2).

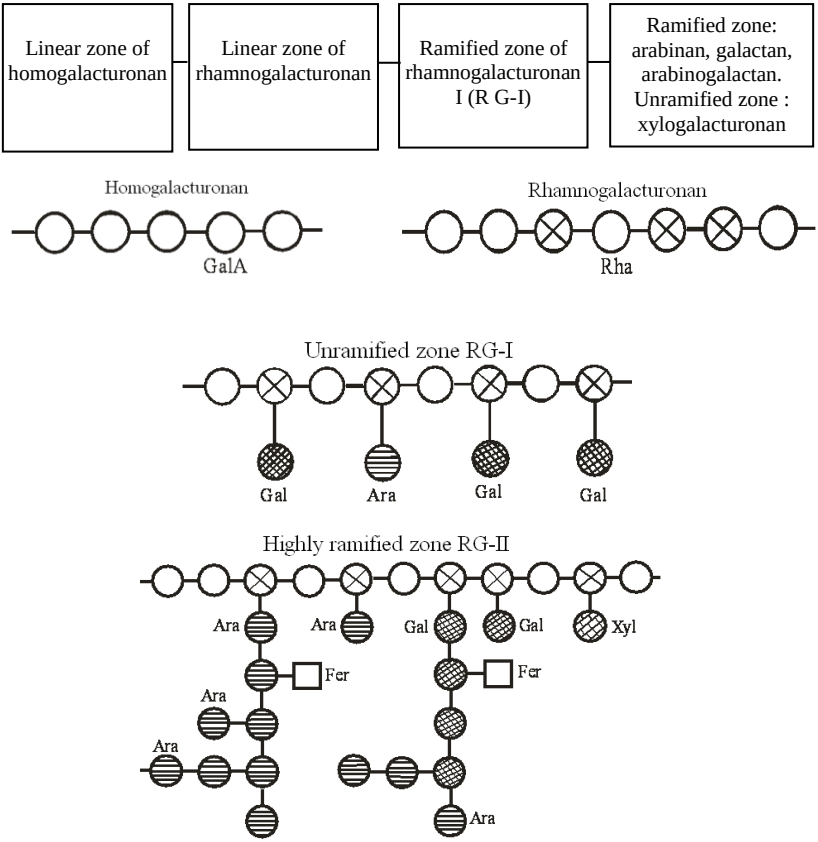


Figure 1.2 – Scheme of pectic polysaccharides construction

Linear area of homogalacturonan consists of 1, 4 – tied remains of α-D-galactopyranosuronic acid. These areas are connected by one or two remains of α-L-rhamnopyranose included into a linear chain by 1,2-bond. The main hydrocarbon chain is constructed in the same manner for many types of pectin. They may differ only in the chain length [12, 15, 17].

An extensive area consists of several subunits: ramnohalakturonana, arabinohalaktana and ksylohalakturonana that may be present in different ratios [77] (Table 1.1, Table 1.2).

Table 1.1 – **Structural elements of pectic substances**

Type of molecules	Main structures
Homogalacturonan	Long homogalacturonanic sections, which are broken by rhamnose. The degree and division of methyl ethers. The degree and division of acetyl groups.
Rhamnogalacturonan I (RG-I)	Neutral sugars of side chains, their nature. Length, sugar type, the degree of side chains saturation. Ramification of side chains, rhamnose proportion: galacturonic acid. the level and division of methyl and acetyl groups.
Rhamnogalacturonan II (RG-II)	Structure conservatism. The level of unique O-Mexylose sugars. Division of neutral sugars in side chains. Correlation of RG-II with other molecules of plant tissue.
Xylogalacturonan	The amount of xylose, length of xylose side chains. Other sugars (fucosa). The degree of methylation and acetylation. The composition and location of side chains.
Arabinan	The size, amount and composition of side chains. Other polymers, connected with arabinan.
Arabinogalactan I	The size, balance of arabinose and galactose, other sugars in side chains, type of connections, division and balance of side chains; the amount of proteins, connection with other pectins.
Amilogalacturonan	The amount of amylose, length of amylose chain, methyl ether, division and binding of side chains.

Table 1.2 – **Correlation of structural elements in pectins of different origin**

Structural elements	Beetroot	Apples
Polysaccharides total content (for dry mass), %	67	20
Pectic polysaccharides total content, %	40	42
Homogalacturonan	29	36
Xylogalacturonan	1	4
Rhamnogalacturonan II	4	10
Rhamnogalacturonan, side chains	8	4
Arabinan	46	27
Arabinogalactan	12	20

Homogalacturonan. Most of industrial pectins differ from each other by their structure. These differences are connected with

the level of esterification in C-6 position and distribution of complex ester bonds in homogalacturonan molecule [58]. Usually the esterification level demonstrates correlation of complex ester bonds per 100 moles of galacturonic acid. Pectins are called high-ester at 50% esterification level and higher, low-ester pectins – at the level less than 50%. Methoxy groups' distribution is rather complicated and changes at different sectors of macromolecule. Their placement on the main channel can differ changing their physical properties. The distribution of ester carboxyl groups can change accidentally and be distributes as blocks in the chain of polygalacturonic acid in a pectin molecule [6]. It is considered that fully esterificated homogalacturonans are created at the initial stages of biosynthesis, and then under the influence of methylesterases or extraction during pectin secretion, their deethoxylation take place [39, 40].

Rhamnogalacturonan. Rhamnogalacturonan are pectic molecules enriched by rhamnose and galacturonic acids, the chains of which contain rhamnose molecules in the positions α-(1→2) and α-(1→4) galacturonosic remains with the length 100…300 RG-1 molecules. The size of RG-1 depends on plant tissues and growth conditions. RG-1 acetified by galacturonic acid in O-3 position was determined in specific conditions of hydrolysis. Acetylation can also take place in O-2 position. Rhamnogalacturonan received in "soft" regimes of extraction always contain some rhamnose and galacturonic acid in the ratio 0,05:1. No attempts to find places where 2 remains of rhamnose could join one remain of galacturonic acid were made.

Depending on the origin of a plant tissue from 20% to 80% of rhamnose are connected with side chains in O-3 or O-4 position. The length of side chains can vary from one to 50 remains of arabinose and galactose. Ferulaic acids can be connected with neutral carbohydrates of beetroot pectin by ether bonds. Taking into account possible combinations, it is possible to make a conclusion that rhamnogalacturonan is a main structure to which other structures of pectin are joined [19].

RG-1 fragment in various pectins can noticeably differ, possessing a main chain from alternate remains 1, 4 – combined galacturonic acid and 1, 2 – combined remains of rhamnose, partially substituted by isolated remains of galactose, which are joined by 1, 4

bonds to the rhamnose remains. Besides, RG-1 subunit can have long chains of arabinan and galactan. Arabinose remains can be terminal. Isolated remains of xylopiranose are joined by 1, 3 – bonds to the main carbohydrate chain (as in the apple pectin) [40]. It can be a fragment of apiogalacturonan, where isolated or 1,3- combined D-anion remains join by 1,2 or 1,3 – bonds to the remains of D-galacturonic acid [19].

The general model for apple, citric and beetroot pectins characterized by the rotation of linear 1,4 – bond chains of α- D-galacturonan and ramified area containing most of neutral monosaccharides [58] is suggested. Pectins outgoing from these sources differ by the molecular mass (citric > apple > beetroot) and by the amount of rhamnose (beetroot > apple > citric). Homogalacturonan is extracted from apple, beetroot and citric pectin with the polymerization level 72 – 120, 91 – 108, 114 – 138 respectively. Remains of ferulaic acid (Fer) joined to neutral monosaccharides of side chains (mostly to the remains of L-arabinofuranose) by a complicated ether connection are found in pectin [25, 39].

Rhamnogalacturonan II (RG-II) [46, 48, 49], minor component of primary cell walls, differ by a very complicated structure. RG-II is stable to the activity of L-1,4-endopolygalacturonase. It is extracted after the background processing of pectins by this enzyme. Monosaccharide remains RG-II are widely spread: D-galacturonic acid, L-rhamnose, D-galactose, L-arabinose, D-xylose, D-glucose, L-fucose, D-mannose and D-glucuronic acid [29].

But alongside of them very unusual monosaccharides were found: D-apiose, 2-0-methyl-L-fructose, 2-0-methyl-D-xylose, acetic acid (3-carboxyl-5-desoxyl-L-xylofuranose, 3-desoxy-D-licso-geptulosaric acid and 2-keto-3-desoxy-D-monno-oktanic acid.

RG-II was first extracted from sycamore [55]. This polysaccharide is found in cytoderm of rice, onion, and kiwi fruit. It is also extracted from beetroot residue, from the conversion product of grape as a main component of polysaccharides in red wine and from the juice of apples, carrots, tomatoes, previously processed by enzymic preparations. RG-II is present in pectic polysaccharides of black currant and blueberry as a dimeric polymer (in cell walls, juice

and pressed skins. In RG-II, which is found near cell cytolemma, the remains of galacturonic acid of the main chain are not etherificated by methanol. At the same time RG-II, localized in primary cell walls, contains a lot of methoxy groups. It is worth noting that after fruit and vegetables breakdown during their ripening, RG-II is becoming dominant polysaccharide in apple, tomato and carrot juices [48]. RG-II is rather small by the size polysaccharide and differs in an extremely complex structure, which has not been identified yet [50].

It is known that RG-II is one of the polysaccharides with borate bridges, which create dimeric polymer [52, 54]. This borate complex is a part of macromolecular pectic complex consisting of homogalacturonan, RG-I, and RG-II. At the same time borate ethers RG-II create molecules of cross-linked macromolecular pectin (Fig. 1.3.). It is quite possible that homogalacturonan, RG-I and RG-II are linked by covalent bindings without borate [53].

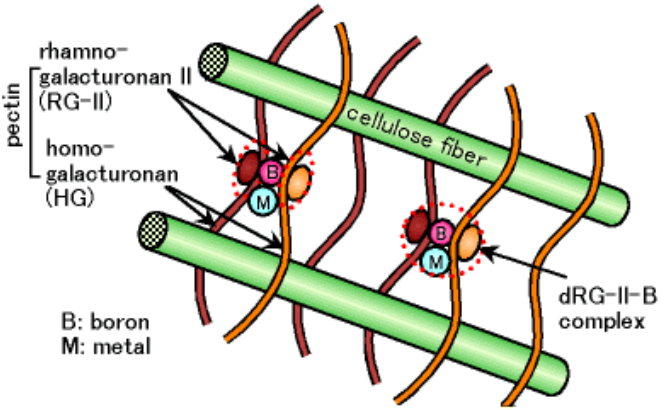


Figure 1.3 – Scheme of the formation of metal-borate complex ramnohalakturonanom II

Arabinans and galactans are usually smaller part of pectic substances in comparison with polyuronic acids. They are neutral polysaccharides. Arabinans are ramified polymers consisting of the L-arabofuranose remains. They are linear chains formed by the connected α-(1-5) linkages of L-arabofuranose remains, to which in turn side single L-arabofuranose remains are joined by α-(1-3) linkages [74]. Galactans are large flat chains formed from D-galactopyranose remains bound by β-(1-4) linkages. In a primary cell

wall arabinan and galactan are so tightly associated that first they were described as a unified poilysaccharide called arabinogalactan. According to modern notions, some chains of arabinan are connected with the chains of galactan by a glycosidic a-(1-4) linkage [74, 76].

Arabinans are the component of homogalacturonans. α-L-(1→5) bound arabinose remains are their basis, which are naturally bound with the remains of α-arabinosil in the position O-2 and/or O-3. Such grouping can include single arabinosils but there are also prolonged variants of these compositions.

Side arabinosil chains can be composed of arabinogalacturonic remains, which are usually covalently linked with the areas saturated with galacturonic acids. Arabinans are met in cell walls of apples, beetroot, turnip, carrot, etc. molecular mass of arabinans is more than 10 thousand a.m.u.(atomic mass units). It is rather difficult to liberate pure arabinans either chemically (by β-elimination) or through enzymatic splitting.

Galactans and arabinogalactans, in which arabinose and galactose remains are the main structural unit, were found in many plants. They are classified to arabinogalactans of the first and the second type, in which galactans are presented as various proportions of side chains of pectin or independent polymers [74]. Arabinogalacturonan of type II can include the remains of protein molecules as side chains and be called proteic arabinogalacturonan (PAG).

Arabinogalactans I are a large group of polysaccharides, found in plant tissues, contain (1→4) linear chains of β-D-galactopyranosyl remains. Pure galactans were extracted from lupines, potatoes, and tobacco. Their molecules looked like short chains α-(1→5) arabinofuranosic remains bound in the position O-3. Also O-6 bonds of galactonic basis with β-galactose are met.

Depending on the extraction type, pectin remains can be connected with arabinogalactans in the position O-6. We managed to extract arabinogalactan from beans. By means of the methods of chromatography and mass-spectroscopy the presence of non-characteristic sequences (1→4) bound galactose remains, which carry arabinose remains and linear oligosaccharides in the end of macromolecule. They consist of (1→4) galactose remains with α-(1→5) arabinofuranosic remains included into their structure [73].

Arabinogalactans II are greatly ramified polysaccharides with the chains of β-D-galactopyranose remains joined to them in the position 1→3 and 1→6. They are most often met in the leaves, stems, roots, flowers and seeds.

The main structural element of galactan II is β-(1→3) galactose. β-(1→6) galactopyranosic remains can end in L-arabinosic remains. (1→3) galactan can be connected with arabinopyranose and with α-(1→3) arabinose ramifies. In general, galactose remains are more often met in side chains than those of arabinose, though proportion of arabinose to galactose can change [29]. Arabinogalactans II can be found in inside the side chains of pectin molecules. As it was stated above, they can be connected with arabinogalactonic proteins, which is used for the reception of glue from some sorts of acacia (Acacia senegal).

The proof of the construction and mutual location of the chains of pectin molecule was received by means of the method of molecular modeling [34]. Arabinogalactonic side chains are found at an angle of 50^{o} to the main chain of rhamnogalacturonan. Arabinogalactans I are placed orthogonally to the main chain of rhamnogalacturonan that results in the construction of twisted chains with a high level of symmetry. Side chains (1→3), bound with β-D-galactans II, have low level of symmetry. Arabinan ramifications fill in empty spaces in a spun pectin molecule for the formation of additional bridges O-3 and O-2 arabinan chains. Arabinan side chains of arabinogalactan I can twist round the main chain and bond with each other, creating rhamnogalacturonans. Modeling of arabinogalacturonan II demonstrates that no steric changes happen even if infinitely long (1→3) β bound galactan chains connect with infinitely long (1→6) galactan side chains, which, in its turn, are connected by (1→3) α-arabinofuranose [74].

Xylogalacturonan. Xylogalacturonan is received during the enzymatic treatment of a plant tissue and consists of linear chain of homogalacturonan with single droplets of xylose, bound with galacturonic acid in the position O-3. The amount of β-xylose is different depending on the origin. The amount of methylated fragments in xylogalacturonan can greatly differ [43].

Amylogalacturonan. Amylogalacturonans are found in duckweed and have two kinds of mono- and diapyosic chains joined

to galacturonic basis, but there is little information about their division on the main chain of a macromolecule.

Therefore, taking into account the structure, pectic substances include galacturonans, rhamnogalacturonans, arabinans, galactans and arabinogalactans.

Because polysaccharides containing D-galacturonic acid are the main components of pectins, their properties are the features of a whole group of pectic polysaccharides reflected on physical-chemical properties of pectin and pectin products.

1.2.2 Characteristics of industrial pectins

Pectins are mainly homogalacturonans containing some neutral side chains. They are extracted in the process of acid extraction of vegetables and fruit (beetroots, apples, citrus), and constitute a group of commercial pectins [59]. According to European standards for food products, commercial pectins should contain more than 65% of galacturonic acid remains on dry mass, and according to American pharmacopoeia – more than 74%. Homogalacturonans differ from each other in the following: galacturonic acid remains may contain free carboxyl groups or those etherificated by methanol (LE – the level of etherification r methoxylation). In the positions C2 and C4 – Gal A remains can be acetilized but this is true for pectins in beetroots and potatoes. In order to intensify gel-creating properties, pectins with low LE (LM-pectins) chemically amidate by ammonia in methanol that leads to the appearance of amide groups in the position LE remains of Gal A (LMA – pectins, amidated pectins) [56, 57].

Physical-chemical properties of commercial pectins depend on their molecular of commercial pectins depend on their molecular mass and level of etherification. The level of etherification is determined by the amount of moles of methanol per 100 moles of galacturonic acid [69].

Pectins with the high level of etherification (HEP) contain 50% and more of etherificated GalA remains. Low etherificated pectins (LEP) receive deetherification of HEP in the determined controlled conditions (pH, temperature, duration). Both groups of pectic polysaccharides form jellies, though in different conditions: LEP under low pH indexes or at the presence of calcium cations but

HEP – due to hydrophobic interactions, especially in the presence of sucrose [67, 68, 69].

Highly etherificated pectins. Highly etherificated pectins are the pectins with the level of etherification higher than 50%. Main types of HEP used in the production of marmalade, jams, jellies, and fruit candies are presented below (table 1.3).

Table 1.3 – Types of highly etherificated pectins

Types of HEP by the velocity of jelly formation	Jelly power (º USA-SAG)	The level of etherification, %
Rapid set	150±5	69-73
Medium set	150±5	64-68
Slow set	150±5	59-63

The level of low etherificated pectins etherification is less than 50% (fig. 1.3).

Commercial low etherificated pectins are mainly produced from plant material containing highly etherificated pectin. Deetherification of highly etherificated pectin into low one occurs in weak solutions of acids or alkali [85].

Use of ammonia in alkali process of deetherification results in the eception of the so called amidated low etherificated pectin, which contains galacturonamidic chains in a molecular chain alongside with galacturonic acids, methyl ethers of galacturonic acid [50, 60].

Low etherificated pectins. Main types of LEP used in the treatment of fruit are presented in table 1.3 [35].

Table 1.4 – Types of low etherificated pectins

Type of LEP	Reaction on calcium	Relative velocity of jellification	Jelly thickness	Level of etherification	Level of amidation
Rapid set	high	fast	120±5	30	20
Medium set	average	average	100±5	32	18
Slow set	low	low	100±5	35	15

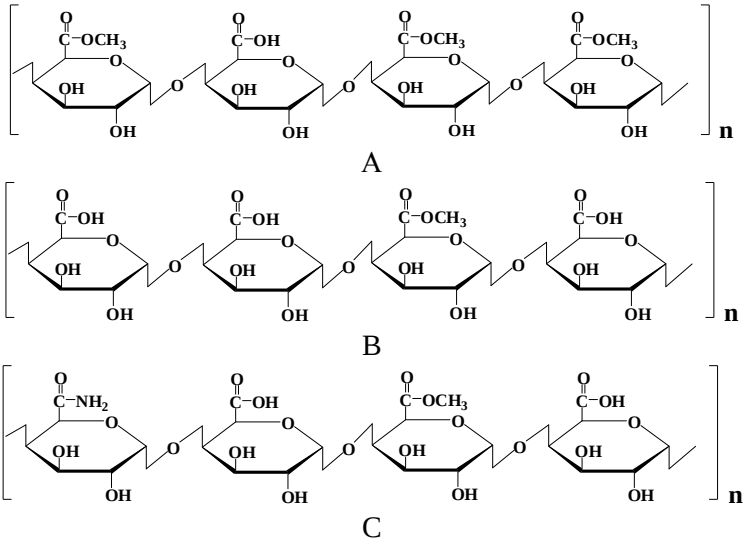


Figure 1.3. – Chemical structures of main kinds of industrial pectins: A – highly etherificated pectin; B – low etherificated pectin; C – amidated pectin

Marc of citrus and apples – a by-product during juice production, and sugar-beet residue – waste products of sugar production from sugar-beet – are usually used for the reception of commercial pectins.

Pectins from waste products of sugar beet processing are characterized by low gel-forming ability because of low molecular mass and high content of acetylic groups. Treatment by acid methanol removes acetylic groups and increases LE but substantially reduces molecular mass [63]. Acetylic pectins find application due to emulsifying properties [62].

Commercial pectins are widely used as thickening agents, gel-forming, adhesives, emulsifiers and stabilizers of the solutions due to their valuable physical-chemical properties.

1.2.3 Functional and technological properties of pectin

1) *Solubility and viscosity of pectin*

Pectins, like other gelling agents, are not soluble in the environment with the existing conditions for gel-formation [82].

Water is the best solvent of pectic substances. They are also dissolved in 84 % phosphate acid and liquid ammonia; in glycerin and formalin they expand. In other organic and inorganic solvents they are practically insoluble. In other organic and inorganic solvents they are practically insoluble [3, 24].

Solvency of pectin depends on the level of polymerization and etherification. Solvency in water increases with raising the level of etherification and reduction of the size of molecule. Pectic acids deficient in methoxy groups are insoluble in water even with small molecular mass. It is easier to dissolve pectin from two pectins with different molecular masses with the shorter chain but bigger amount of methoxy groups. To receive homogeneous solution it is necessary to grind the powder of pectin with sugar or wet with the spirit. At indoor temperature it is possible to receive water solutions containing less than 3 % of pectic substances.

The easiest method to dissolve the powder of pectin is to mix it dry with 5 parts of sugar by means of a mixer with the churn rate of turn-over 20…30 rpm. The received mixture is easily dissolved in water. It is recommended to boil suspension for one minute till full dissolving. Most of the sugar should be added only after pectin is dissolved, because solubility of this polysaccharide falls while the amount of dry substances grows.

Viscosity is one of the important characteristics for pectic substances as well as for other lyophilic colloids. Molecules of pectin are easily associated with each other or with large molecules of accessory agents. Pectins do not diffuse from the solutions through cell membranes of the plants, which is connected with their belonging to high-molecular substances. These properties are used for the separation of low-molecular substances. These properties are used for the separation of low-molecular substances from pectic substances, for example, in the process of sugar diffusion.

Molecules of pectin are to be solvated, i.e. hydrated film is formed. It is denser in the interior layers and less dense in the sectors expelled from the particles of polymer. Mutual disposition of pectic molecules can change depending on chemical nature of lyophilizate, solvent, temperature, etc. High relative viscosity sharply growing with the concentration increase, structural or anomalous viscosity is characteristic for the ashes of lyophilic colloids [15].

Viscosity of water solutions of pectin depend on various factors: concentration, length of molecular chain, level of etherification, presence of battery acids and temperature. With the increase of molecular mass viscosity increases all other things being equal. Viscosity increases with the increase of electric charge of macromolecule (the amount of free hydroxyl groups) with the same meaning of the molecular mass. The investigations carried out with pectic substances showed that pectic solution behaves as a solution of bunch of elementary fibrils in the interval of pH=3.5–8.0, viscosity is maximal with pH=6–7, with pH=4 – viscosity is minimal. Addition of some amount of sodium chloride or its salts to the solution of pectin results in noticeable reduction of viscosity, and then the latter gets constant meaning.

High relative viscosity can be explained by the solvation. To explain structural viscosity the hypothesis about the existence of a net of joined particles inside the ash was suggested. Elastic powers of colloid "net" obstruct the ash flow along the capillary of the viscometer. This stipulates most of viscosity than for non-structured ashes of the same concentration. If elastic structure breaks under the pressure, viscosity of the solvent falls very fast [79].

When the amount of solvent and temperature change, equilibrium between solvation of chain molecules and their mutual association shifts. When the temperature rises, viscosity falls because of the destruction of permolecular structure of pectic substances. When sugar or spirit is added, mutual association of pectin molecules grows, stable aggregates of molecules form, and ash changes into gel. In the process of pectic gels thickening structurization takes place permanently that is followed by gradual raise of relative viscosity of the system.

Viscosity of pectic solution can be determined by means of measuring molecular mass of pectin or its thickness. Ions of calcium increase viscosity of pectic substances solutions that is why the latter is determined in the systems, which do not contain this ion [80, 81].

Measuring viscosity of pectic substances is used for the determination of the molecular mass of pectic substances.

2) *Acid-base properties of pectin*

Under the influence of acids natural protopectin dissolve even at low temperatures. Mechanism of this action has not yet been

clarified. Some scientists state that acid removes polyvalent cations from protopectin; the others are sure that hydrolysis of the cellulose-pectin complex take place.

Under the influence of mineral acids pectic highly etherificated acid hydrolysis even at room temperature, when the temperature rises – the process accelerates. The speed of acid hydrolysis can rise to the level when destruction of pectin prevails.

It is determined that pectic substances entirely destroy in a pectic extraction received from beetroot press cake at temperature 78...80 °C and pH=0,8...1,0 for 12 hours.

Reaction of pectin interaction with acids is widely used for industrial reception of gel-forming pectin from plant raw material, pectic gum and D-galacturonic acid. Various mineral (chloride, nitrate, phosphate, etc.) and organic (dihydroxysuccinic, citric, lactic, etc.) acids are used for the hydrolysis of protopectin.

Hydrolysis of glycosidic linkage results in the depolymerization at low pH value. In most cases L-rhamnose-glycosidic bond split with the formation of galacturonoglycanic chains with the polymerization level 25. It is worth mentioning that under acidic hydrolysis pure elimination of ramified fragments doesn't occur, even if they are formed by L-arabinofuranosolic remains. This process is always followed by depolymerization of rhamnosic bonds.

Hydrolysis of etheric groups is catalyzed not only by acids but alkali as well. Alkali invoke deetherification of molecular chains that is followed by the reaction of β-elimination. With pH=5 pectin solutions are stable only at room temperature. When the temperature rises, hydrolysis of complex etheric groups is followed by splitting of polymeric chain. β-elimination occurs only in glycoside bonds near the etherificated carboxyl group. With pH=6 deetherification and depolymerization accelerate even at room temperature, rate of these reactions increases with pH growth. During the increase of the temperature pectin molecule destroys intensively [4, 15, 24].

3) *Complex formation of pectins*

One of the important properties of pectic substances is their ability to complex formation, which is connected with the interaction of the pectin molecule with ions of heavy and radioactive metals. This quality allows recommending pectin to be included into the diet

of those who are on radionuclides-contaminated territory and contact with heavy metals. The most dangerous for a human organism are stable isotopes of cesium, strontium, yttrium, etc. excretion of pectin respectively to the dose of Cs^{137} is 8,4 %, Sr^{90} – 52,6 % [97].

Complexing properties of pectic substances depend on the content of free carboxyl groups, i.e. the level of etherificating these groups by methanol. The level of etherification determines linear density of the charge of macromolecule, and, respectively, the power and method of cations links.

At the high level of pectin etherification (more than 90 %) free carboxyl groups with the included atoms C6 are distant from each other. Herewith, calcium or strontium salts of pectic acid dissociate. With the reduction of the level of etherification, i.e. with the increase of the charge of macromolecule, the links of pectic substances with cations grows, and pectates stability constant increases according to the function close to logarithmic dependence. At the etherification level 40 % information changes that leads to the aggregation of pectic macromolecules and creation of strong internal molecular chelate bond.

Ability to complex formation doesn't depend on molecular mass of pectin and is determined by the selectivity of cation exchange coefficient. It is characteristics of pectic substances saturation by two-valent cation. Investigation of sorption ability of pectic acid showed that cations can be ranked into one line $Mn^{2+}>Cu^{2+}>Zn^{2+}>Co^{2+}>Pb^{2+}>Ni^{2+}>Ca^{2+}> Mg^{2+}>Cd^{2+}$ by the ability to complex formation and activity. Such sequence is explained by the fact that cations Mn^{2+}, Cu^{2+}, Co^{2+} i Ni^{2+} besides the compositions of $R(COO)_2Me$ type form compositions of different type (except carboxyl ones) due to the interaction with oxygroups of macromolecules or due to the formation of salt like $R(COO)Me(OOCCH_3)$ [98].

Ability to complex formation of pectin depends on pH of the environment. At various values of pH pectic substances have various values of this ability. High ability to complex formation for pectin from beetroot press-cake is achieved at pH=5 (505,0 мг Pb^{2+}/g) i pH=10 (503,7 мг Pb^{2+}/g). At such values beetroot pectin bound up to 64…68 % of total amount of the introduced strontium. For pectin of

sunflower the biggest ability to complex formation is observed at pH+9 (455,0 мг Pb^{2+}/g), apple pectin - pH=5 (312,2 мг Pb^{2+}/г).

Thus, optimal value of the environment pH for each type of pectin, when maximal complex formation takes place, is individual and depends on the type of pectin-containing raw material. High ability to complex formation in all pectic substances occurs in the range of pH=4…12. Maximal values are achieved at pH=5 and pH=9.

In the literature different data concerning the influence of quantitative ratio metal-pectin on the ability to complex formation are met. The conducted investigations allowed us find out that in more dissolved solutions in comparison with the concentrated ones, pectin demonstrates bigger ability to complex formation, though with the increase of concentration ability to concentrate should grow proportionally for all pectins. This must be connected with mutual blocking of carboxyl groups [99].

Significant impact on the ability to complex formation belongs to the paired effect of pectin and salts of heavy metals. Simultaneous reduction of pectin concentration in the solution with the increase of heavy metal concentration in it leads to the significant increase of the linkage constant. Thus, during the interaction of 1 part of cobalt with 10 parts of sunflower pectin in the solution 7.8 % of metal is bound, and at the proportion 1:100 – 80,2 % similarly at the reduction of concentration to 0,5 % of beetroot pectin it bonds 75 % of strontium.

Due to the ability to complex formation in relation to metals pectin is an essential agent in manufacturing food products with preventive and therapeutical effect. Optimal daily preventive dose of pectin equals 2…4 g for those contacting with heavy metals, and in the conditions of radiation pollution – 15…16 g [96].

4) *Influence of enzymes on pectic substances*

Splitting of pectic substances under the influence of enzymes is of great practical importance and is widely used in the processing of beetroot and clarification of juices and wines. It is known that under the influence of hydrolytic enzymes reactions take a course by the following scheme:

$$RR1 + H\text{-}OH \leftrightarrow RH + R1OH.$$

During enzymatic hydrolysis the process of creating enzyme-substrate complex, which undergoes interior-molecular rearrangement under the influence of active center of the enzyme takes place. Anhydride bond breaking of the catalyzing substrate leads to the excretion of one of the reaction products from enzyme-substrate complex. The other product excretes after rearrangements connected with adjunction of the water molecule.

Pectin- esterase, endipolygalacturonasa, exopolygalacturonasa take part in the process of enzymatic hydrolysis of pectic substances [38, 65].

Enzymes from the lyase of pectintranseliminase class canalize non-hydrolytic breaking of pectin.

Pectolytic enzymes are classified according to the Commission on the development of enzymes nomenclature [69].

Pectin-esterase (polymethylgalacturonatesterase, EC 3.1.1.11) de-etherificate pectin with the creation of pectic acid as a result of methoxy groups extraction. Pectin-esterase synthesize by higher plants, microscopic groups and bacteria. They possess high specificity to methyl ether of pectic acid. Noticeable reduction of enzyme activity is observed with a gradual demethoxylation of pectin. Mycogenous pectin-esterase is very active at pH 5,0…6,5 and temperature 50 ºC for 60·sec.

Endopolygalacturonase (EC 3.2.1.15) hydrolyses α-(1-4)-bonds of pectic acid by free, unregulated method. The enzyme is produced by microorganisms and higher plants. The level and velocity of hydrolysis fall with the increase of the level of pectic acid etherification, because free carboxyl groups raise activity of the enzyme. Enzyme activity falls with the reduction of the length of oligogalacturonans chain.

Exopolygalacturonase (EC 4.2.2.9) hydrolyses pectin successively breaking bonds from non-reduced end of the substrate. Mycogenous exopolygalacturonases are maximally active at pH 4…6 and create monogalacturonic acid as a final product. Bacterial enzyme with *Erwinia aeroideae* acts at pH 7,2 and di-galacturonic acid is a catalyzate.

There is information that pectin bonds are endopolygalacturonasa, hydrolyzing α-(1- 4). But existence of this

enzyme has not been finally proved: it is possible that polygalacturonasa preparations cointaining pectin-esterase are taken as polymethylgalacturonasa.

Also if the substrate has not been etherificated in full, pectin may possibly be hydrolyzed by polygalacturonasa in the zones that do not contain methoxy groups.

Endo- and exopolygalacturonatlyases, polymethylgalacturonatlyases are referred to the class of lyases influencinf pectic substances.

Endopolygalacturonase (EC 4.2.2.2) unregulatedly, freely breaks bonds of pectic acid in the reaction of translimination. Optimal value pH=8,0…10,0. One of the main features of pectolitic lyases is their activation by the ions of calcium.

Exopolygalacturonase (EC 4.2.2.9) successively breaks pectic acid from non-reduced end of the substrates molecule in the reaction of transelimination. Optimal pH values for these enzymes equal 8,0…9,5.

Endopolymethylgalacturonatlyase causes voluntary breaking of pectin in the process of transelimination. This is the only known enzyme directly hydrolyzing pectin. Mushrooms and some bacteria are the main producers of this enzyme. Depending on the producers optimums of pH action of enzymes fluctuate from 5,5 to 8,3. Highly etherificated pectin is the best substrate for endopolymethylgalacturonatlyase, polygalacturonic acid and pectic acid amide are not hydrolyzed by the enzyme. Endopolymethylgalacturonatlyase activity falls very fast alongside with the reduction of the chain length.

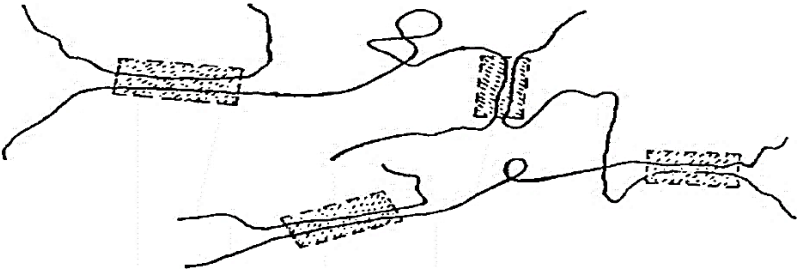
Pectolytic enzymatic preparations are widely used in food industry for maceration of plant raw materials, reduction of density in juice concentrations, clarification of juice, etc.

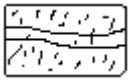
It is important to prevent factors of enzymatic destruction of pectic substances. It is possible to use enzymatic preparations liberated from pectolytic enzymes for the preparation of pectin-containing raw materials.

1.2.4 Nature, mechanisms of gel formation

Modern theories of pectin gel-formation suppose presence of specific zones, created from unsettled joined pectin chains, in the

molecules of pectin. There are fragments of free unbound with each other chains by side with these zones. It is the result of the presence of acetylic groups, rhamnose and side chains. Such structure behaves as a side net and simultaneously obstructs the creation of insoluble chains (fig.1.6).





– typical, bound sections created from the ordered pectic chains.

Figure 1.6 – Structure of pectin gel.

Filamentary molecules of pectin form three-dimensional carcass in the presence of various additions (sugar, acid, ions of calcium) in the process of gel-formation [85, 86].

The most conventional is the theory of creating gels of pectin, which grounds on the following assumptions:

- pectin is a hydrophilic colloid;
- sugar is considered to be dehydrating factor;
- application of edible acids helps reduce negative charge of a pectin macromolecule that creates conditions for relative rapprochement of molecules and emergence of hydrogenous bonds;
- dehydration process of pectin macromolecules and formation of hydrogenous bonds between them runs for some time as well as the processes in other polymeric systems;
- pectin dehydration velocity grows while concentration of hydrogen ions increases;
- maximal strength of gel is registered at ion balance.

Gel formation depends on molecular mass of pectin, etherification of its molecule and content of functional groups, sugar concentration in the solution, amount of ballast substances accompanying the pectin, temperature and pH of the environment [92].

With the account of the level of etherification of pectin molecule two types of gels are differed: with side and basic valence.

Acid-sugar pectic gels are formed due to hydrogenous bonds with the participation of undissociated free carboxyl groups. Such type of gel is characteristic for highly etherificated pectins. Low etherificated pectins form gels only in the presence of ions Ca^{2+}. Therefore, molecules of pectin interact due to free carboxyl groups, which are bound by Ca-ion to strong carcass. Such jellies are called ion-bound. Besides the main jellies it is possible to form intermediary ones, containing both sugar and Ca-ion. Such jellies are characteristic for pectins with the level of etherification about 50%, e.g. for beetroot pectin [91].

Depending on the conditions when gel is formed, its structure is formed at different quantitative participation of various bonds. The acid added for gel formation pushes out cations from pectin molecule, forms free carboxyl groups, reduces their dissociation neutralizing electrostatic forces of repulsion between the molecules of pectic acid. The strongest jellies are formed in the presence of citric, dihydroxysuccinic and trioxyglutaric acids.

Sugar plays the role of a dehydrating agent in the process of gel formation. The ability to dehydration in various sugars – sucrose, glucose, and maltose – is different, and specifies the character of their influence on the density of pectic solutions. The biggest strength of gel is achieved at adding sucrose, the smallest – at adding maltose.

To create gel in a three-component system pectin-sugar-acid their optimal proportion is required. It is not absolute but depends on the type of pectin that determines the limits of proportion of the components in a formulation mixture. In practice optimal condition is approximate proportion pectin:sugar:acid – 1:60:1.

Gel formation of pectin depends on pH of the environment and temperature of the process. Maximal strength of gel for highly etherificated pectins is achieved at pH=3,0…3,3, for low etherificated – at pH=2,5…2,8. pH reduction on 1/10 in predetermined conditions of gel formation can cause raise of optimal temperature on 5 ºC.

It is worth noting that despite stating in a literature optimal pH value for getting maximally strong jellies, there is no scientific explanation of connection pH and pectin ability to gel formation.

Chemical construction of the molecule of pectin substantially influences gel formation. Pectic acid, in which the remains of galacturonic acid have carboxyl groups, is water-insoluble and isn't able to form gel. Ballast substances linked with pectin by valence bonds (e.g. with other polysaccharides) causes conformation of its macromolecule and negatively influences gel formation and its strength.

Acetyl groups bound with hydroxyl groups sufficiently worsen their ability to gel formation. Most of acetyl groups are found in beetroot pectin (0,38…0,80 %), pectin of sunflower anthodium (0,45…0,90 %), stipulating their low ability to gel formation.

We studied the possibility of increasing the properties of beetroot pectin to gel formation chemicalizing them with reagents. Use of ammonium persulfate or hydrogen peroxide lead to the increase of the molecular mass of soluble pectins due to restoring sewing together and is followed by the formation of strong gel. Jellies received in such a way possess high water retention capacity and can be widely used in food industry.

1) *Sugar-acid pectic gels*

Association of pectic chains leads to the formation of three-dimensional spatial structure, i.e. to the formation of gel. Two or more sectors of the chain are placed alongside and interact. The issue is about the long sectors of the chains with uniform sequence, which are broken by the inclusion of rhamnose and ramifications. There are some types of chains' associations, which are determined by the level of etherification. Gel formation for highly etherificated pectins is stipulated by two main factors:

1. addition of sucrose or other sugars leads to dehydration of pectin molecules that simplifies rapprochement of polymeric chains and makes the creation of mudflow structure via hydrogen bonds.

2. reduction of pH of the environment depresses dissociation of free carboxyl groups and reduces electrostatic repulsion between the chains. The described mechanism was earlier described in the literature as "sugar-acid gel formation".

Nevertheless, the latest results of the investigations prove that pectins with high level of etherification are stabilized in gel by the combination of hydrophobic interaction and hydrogen bonds; that is why the notion "sugar-acid gel formation" is to be explained in detail.

Methyl ether groups are hydrophobic particles of pectin molecule. Under the influence of hydrophobic powers they group to aggregates, trying to have the smallest surface of the contact with water. Besides hydrogen bonds, e.g. between the non-etherificated carboxyl groups are formed when pH value of the gel is rather low and dissociation of carboxyl groups is suppressed.

In general, hydrogen bonds stabilize pectin net, but without hydrophobic interactions of methoxy groups of gel formation wouldn't occur because of energetic reasons. The higher is the level of etherification, the bigger is the input of hydrophobic powers into gel formation. The part of hydrogenous bonds, which are created via free non-etherificated groups, reduces. If pH value is too high, the influence of negative factors ($-CCO^-$) reduces; if pH value of the product is very high, dissociated carboxyl groups hinder the formation of spatial structure. This influences the interval of pH values for gel formation. Depression of dissociation at very high levels of etherification will not be sufficient. The higher is the level of etherification, the bigger is pH value, at which gel formation begins. Fully etherificated pectins do not need acid for gel formation.

The necessity of high sugar concentration for gel formation of pectins with high level of etherification can be explained by the fact that some sugars stabilize hydrophobic interaction [90].

Figures 1.7, 1.8 demonstrate mechanism of gel formation for highly etherificated pectin with the addition of neutral sugars (e.g. sucrose) to the system. Its addition results in dehydration of pectin molecules found in the solution and allow chains of pectin approach each other to let molecules cross connect through hydrogenous bridges. pH reduction lets avoiding dissociation of free carboxyl groups that, in its turn, leads to the reduction of repulsion of negatively charged pectic chains.

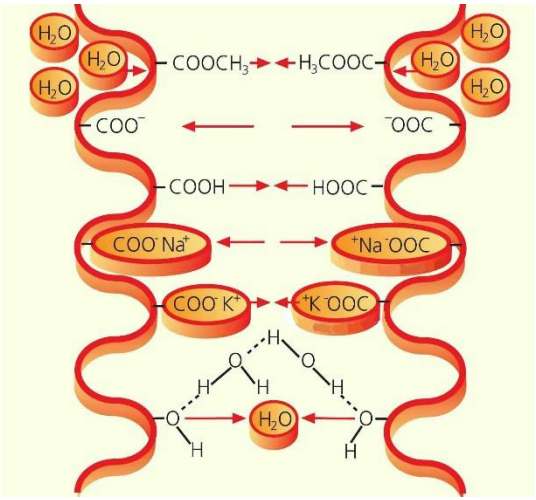


Figure 1.7 – Mechanism of highly etherificated pectin gel formation in sugar-pectic solution

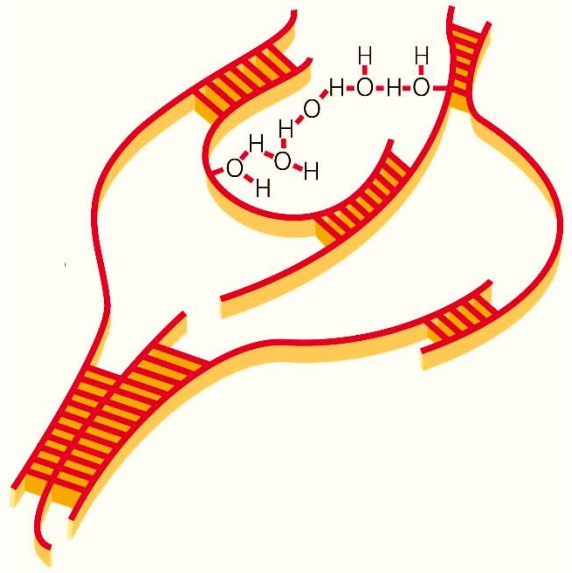


Figure 1.8 – Formation of hydrogenous bridges and hydrophobic interaction during gel formation of highly etherificated pectin.

Gel formation by highly etherificated amidated pectins. Generally formation of gel by highly etherificated amidated pectins occurs at the presence of sugar and acids (sugar-acid mechanism), and doesn't differ from the mechanism of gel formation by highly etherificated not amidated pectins. The presence of amidated groups in hydrated condition in a pectin molecule leads to some spatial changes in the beginning of the reaction. It slows down the creation of the associates between the molecules of amidated pectins in a greater degree than during the gel formation of pectins with high level of etherification. During the final reaction amidated groups additionally stabilize gel structure creating hydrogenous bridges. This results in the formation of strong gel with the elastic-viscous structure.

2) *Calcium-pectate gels*

Mechanism of gel formation for low etherificated pectin sufficiently differs from the mechanism for highly etherificated pectin (fig, 1.9, 1.10). In order gel formation could take place in the system with low etherificated pectin, the governing factor should be the presence of ions of calcium. These pectins form gels at much smaller content of dry substances than highly etherificated pectic substances. Also they allow much bigger fluctuations of pH, which do not influence gel formation. Unlike highly etherificated gel, the one on the basis of low etherificated pectin fuses during heating.

It is evident that conditions of gel formation of low etherificated pectic substances do not suit highly etherificated pectins, though there are common features in the behavior of macromolecules and their properties. Low etherificated pectins, like highly etherificated ones, form interchain permolecular structures only due to carboxyl groups linked with each other by "calcium bridges" [87].

Single rings in polysaccharide chain are rather strong, and all spatial changes in the chain are promoted by the angles of ψ and φ rotation around glycoside bonds. During X-ray-structural analysis all angles in negative pectin and calcium pectates were 79° (φ) and 90° (ψ). These angles form 3_1 coil in distinction of 2_1 characteristic for polygalacturonic acid. In the solution tertiary structure doesn't form because interaction of polymer and solvent leads to redistribution of φ- та ψ-formations. The structure of the molecule turns into

zigzagging. The mechanism for gel formation of low etherificated pectin is associated with a well-known structure called “eggs-box”. Intermolecular interaction goes on by the mechanism side-to-side of interacting galacturans with the formation of parallel bonds between adjacent chains, which are linked internally by molecular electrostatic powers and ion bonds across carboxyl groups [91].

The strength of bonds depends on the power of electrostatic interactions. These bonds are strong if seven carboxyl groups placed in succession are involved into interaction. Etherificated groups in the zone restrict gels formation. All low etherificated pectins form permolecular structures by the common principle [82].

The other important condition for gel formation of low etherificated pectin is high molecular mass. Gel’s strength is determined by the amount of effective interior chain interactions. The smaller is the molecular mass, the shorter is the chain and the stronger is gel. The influence of Ca^{2+} ions on the ability of pectin to gel formation is practically invisible, if 40 % and more of carboxyl groups are etherificated. Calcium remains are most effective in those sectors of molecules where from 15 carboxyl groups placed in succession, 7 are not etherificated.

Presence of monosaccharides of the rhamnose type in a primary structure spatial position of which is incompatible with the geometry of the zones of galacturonic acid linking negatively influences the gel formation. In citric and apple pectin the remains of these sugars are included into side chains. These chains complicate spatial orientation of the molecules required for the formation of the interaction zones.

Interaction of pectin with the ions of calcium complicates with the presence of acetylic fragments in molecules because their size is incompatible with spatial location of chain with a chain inside the interaction zones [51]. It means that presence of acetylic groups reduces ability to gel formation of low etherificated pectins. It is most characteristic for gel formation of beetroot pectin, in which the content of acetylic groups achieves 35 moles per 100 moles of pectin.

Amidating increases ability to gel formation of low etherificated pectin. amidated pectins are less strict to the presence of the ions Ca^{2+} and do not form residual at high concentration of

calcium ions in comparison with other pectins. Amidated pectins well suit the system of gel formation by the type “eggs-box” from the formation of a system of hydrogenous bonds.

Formation of L-pectin gel without sugar weakly depends on pH. It is necessary to add more Ca^{2+} than at neutral pH values for raising ability to gel formation at low pH values (from 3,5). Transition of sol to gel runs faster at neutral pH values due to reduction of dissociated carboxyl groups. At low pH values negative charge of pectin microion is neutralized by the ions of hydrogen that results in the formation of residual.

Increase of ion power of the solution leads to general reduction of the ions content required for gel formation. Under given parameters precipitation of gel of low etherificated pectin containing NaCl, will be stronger than gel without salt. The increase of NaCl concentration promoting the increase of the amount of pectin molecules that, its turn, leads to shortening the length of ion bonds between the polymers explains this effect. At the same time speed of set falls but increases the number of linking zones that helps stabilize gel in general.

Homogenous gels of low etherificated pectins are thermally reverse. The structure of such gels is thermoplastic. Raise of the temperature influences intermolecular bonds. Usually dispersion of such pectin in water solution takes place at the increased temperatures. It is determined that the energy of intermolecular interactions equals 70 $kJ/mole^{-1}$. This is four times higher than for highly etherificated pectin. Due to the reduction of the etherification level and the increase of the amount of pectin and calcium ions the temperature of the sol transition to gel raises.

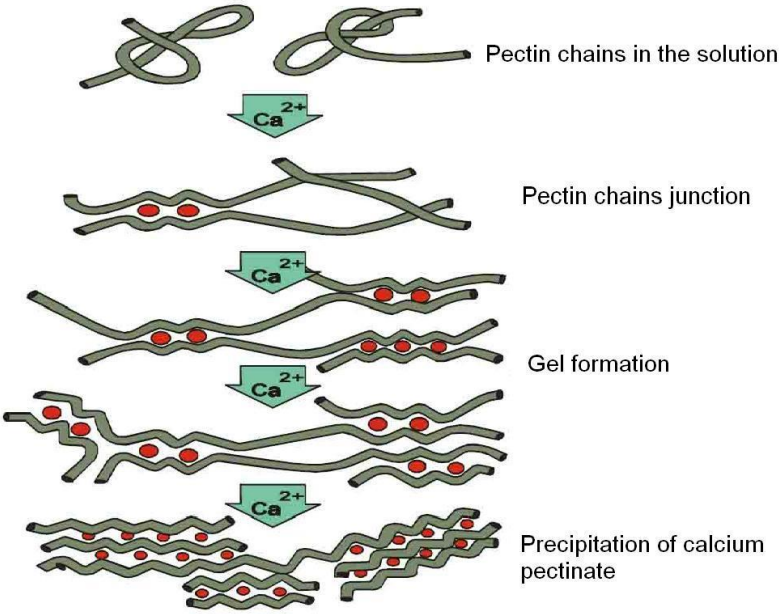


Figure 1.9 – Mechanism of gel formation for low etherificated pectin

Amidated low etherificated pectins normally form gels in jams, jellies, fillings, marmalade even by means of that amount of Ca^{2+} ions that contain in fruit and water. Non-amidated low etherificated pectins use demand the increased amount of calcium to provide gel formation. The level of etherification and amidation determines reaction of some low etherificated pectin on Ca^{2+}. In practice the level of etherification and amidation determines relative temperature of these pectins set. Correspondingly, low etherificated pectins can be classified as those of “rapid set” and “slow set” or as those reacting Ca^{2+}. (fig. 1.11).

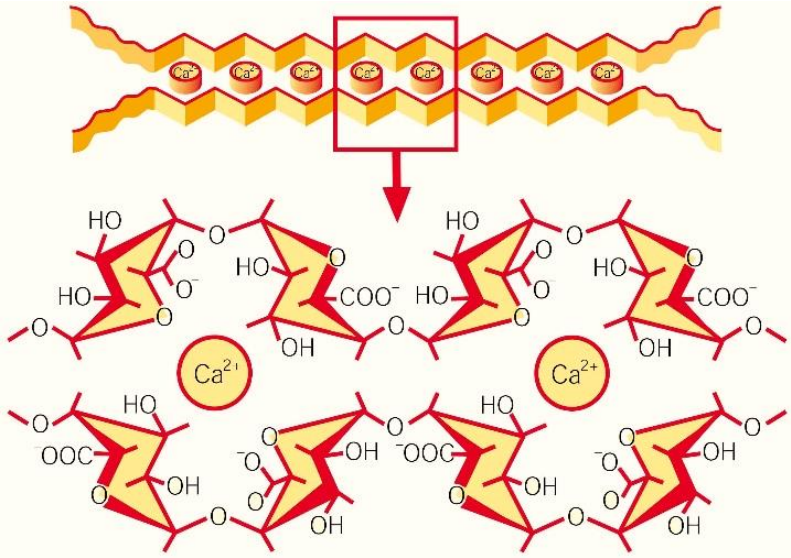


Figure 1.10 – Mechanism of forming the complex with ions of calcium (the so-called "eggs-box") during gel formation of low etherificated pectin.

Combined effect of pH reduction and addition of sugar facilitates gel formation at low content of Ca^{2+} ions. Despite reduction of the number of ionized carboxyl ionized groups, gel formation strengthens due to specific influence of sugar on water activity and hydrophobic interaction in the system [78]. Gel strength depends on the type of sugars. Low etherificated pectins are used in the manufacture of low-caloric jellies with the addition of 30…40 % of sugar [87].

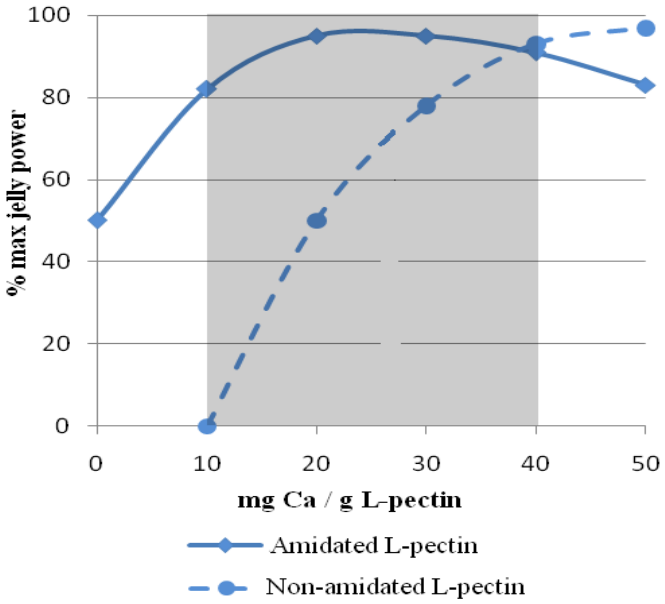


Figure 1.11 – Standard specifications of calcium for amidated and non-amidated low etherificated pectins. Fill area shows "natural" content of calcium in conservation, jams.

Low etherificated pectins are divided into two large groups:

- low etherificated pectins, which de-etherificate by means of acids. Behavior of such pectins during gel formation is described above;
- low etherificated pectins, which de-etherificate by means of ammoniac. During the de-etherification a part of ethereal groups is exchanged to amidated groups. It leads to the change of properties to gel formation in comparison with pectins de-etherificated by acids [61].

For gel formation of both amidated low etherificated pectins and non-amidated ones Ca^{2+} ions and other multivalent cations are needed. The interval of calcium dosing in amidated pectins is bigger, i.e. they form strong gels with a small amount of Ca^{2+} ions. Sometimes calcium is sufficiently concentrated in fruit. High concentration of Ca^{2+} ions is required for premature gel formation. The other difference between amidated and non-amidated pectins

with low level of etherification is the dependence of the gel formation temperature on Ca^{2+} [78].

3) *Pectins gel formation by peroxidase linking*

Reactions with di- and poly-functional compositions, which can crosslink pectin molecules to three-dimensional net structures through linear sectors creating water-soluble, stable, thermo non-reverse gels bound by main valences, are characteristic for pectin. Pectic substances can form derivatives: they are received during interaction of secondary hydroxyl and carboxyl groups.

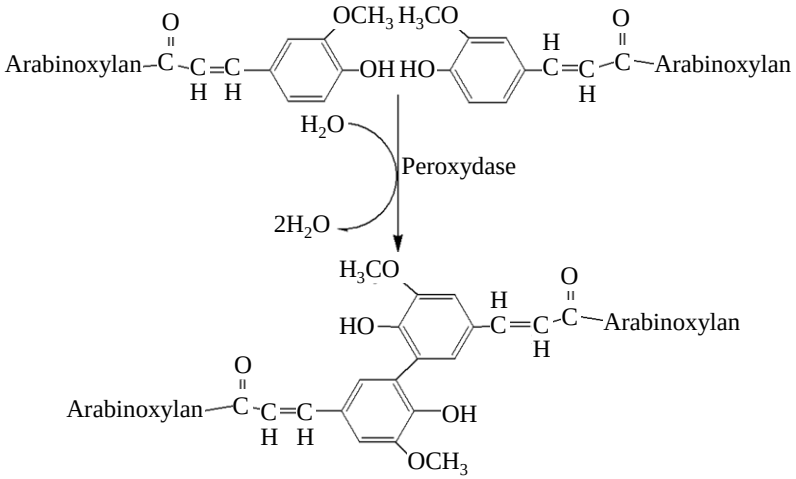


Figure 1.12 – Reaction of peroxide-peroxidase crosslinking of the beetroot pectin structure

It is quite easy to crosslink pectins with formaldehyde (in the presence of chloride acid as a catalyst) as a result of translocation of hydroxyl groups near the second and the third atoms of carbon. Crosslinking is possible between two carboxyl groups of pectin chains at the interaction with erythrodioxide or pyrite [5]. Crosslinking promotes creation of the modified forms of pectin and change of its structural-mechanical properties.

The peculiarity of beetroot pectin is crosslinking by means of peroxidase enzyme and hydrogen peroxide according to the reaction,

the peculiarity of which is interaction of ferulic acid remains in the ramified fragments.

Comparing gels of high- and low etherificated pectins it is worth mentioning that weak from the first view HEP are characterized by rather high values of the module of elasticity and strength. At the same time "looking strong" gels of low etherificated pectins differ in low rheological indexes.

Pectin and pectic, which form gel in the presence of Ca^{2+} or other two-valent cations. This effect is stipulated by the creation of calcium bridges between correspondingly located carboxyl groups. According to Rees energy of such simple electrostatic attractions is very small to consider it an important factor of gel formation.

Both location of carboxyl groups in a macromolecule, and presence of other substitutes sufficiently influence gel formation [87, 88]. Thus, for example, the presence of only one O-acetylic group near C_2 or C_3 per every 8 units of D-galactopiranosuronic acid is able to prevent gel formation. That is why pectins from beetroot and potatoes, which contain a large quantity of O-acetylic remains, are not valuable raw materials for getting industrial pectin as a gel creator.

Location of methoxy groups in pectin chains influences the ability of pectin gel formation. If there are large fragments without methoxy groups interchanging with the zone with etherificated carboxyl groups, such pectins differ in smaller ability to gel formation, which corresponds the level of their etherification.

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2 INVESTIGATION OF STRUCTURAL-MECHANICAL AND PHYSICOCHEMICAL PROPERTIES OF STRUCTURE-FORMING AGENTS

2.1 Investigation of the structural and mechanical properties of agar gels, agaroids, furzellaran, gelatin

2.1.1 Investigation of influence of the organic acids salts and polyatomic alcohols on the strength of jelly of various nature

The current demand of the confectionery and food industries in jelly-forming agents far exceeds their production volumes. The actual problem today is the satisfaction of the manufacturers of jelly products in the structure-forming agents. The jelly-forming ability of red seaweed and gelatin polysaccharides can be enhanced by introducing various additives into the formulation.

This will save some gelling raw materials without compromising the quality of the finished product.

Sufficient strength of finished products at the time of their laying out from moulds is one of the main indicators of high quality products. Other structural and mechanical indicators are also associated with organoleptic evaluation. For example, using the instant modulus of elasticity, one can objectively characterize the “thorniness” or “stiffness” of finished products [1]. Because when chewing or portioning the product is subjected to several types of deformation and destruction (compression, stretching, shearing), acting individually or in combination, it is of practical interest to study of the effect of the proposed modifying additives on such rheological characteristics as elasticity, plasticity, viscosity.

On the other hand, it is known that the strength and structure of the resulting jelly is largely determined by the nature of the bonds that connect the macromolecules into the jelly grid, as well as the possible conformational transformation that can give to the jelly more pronounced elastic or plastic-viscous properties.

In the course of the research, it was necessary to find the optimal concentrations of additives and their combination to enhance

the jelly-forming ability of sulfited polysaccharides and gelatin. The criterion was chosen to determine the mechanical strength of the jelly determined on the Valent device, then was investigated the effect of additives at the established concentrations, on the rheological characteristics of the jelly, and therefore on the nature of the bonds formed and the orderliness of the elements of the spatial structure of the jelly.

According to the accepted sequence of study of the structural and mechanical properties of the jelly, the first stage of the study was to study the strength of gels of polysaccharides and gelatin in the presence of polyatomic alcohols, salts of organic and inorganic acids, sodium carboxymethyl cellulose, and combinations thereof.

The influence of modifier salts on the structural and mechanical properties of different jelly formerming agents has been addressed by many authors [2; 3; 4; 5-7]. Studies have been conducted to determine the strength and rheological characteristics of jelly with the addition of salts to obtain data that can be compared with similar indicators of samples containing polyatomic alcohols (PAA) together with organic acids salts (OAS).

The objects of study were organic acids salts: lactate, acetate and diphosphate of sodium, inorganic acids salts: sodium chloride and chlorine iron, alcohols: ethyl, propyl, butyl, glycerol xylitol, sorbitol and mannitol, 4% jelly of agaroid, 2%- furcellaran, 1% - agar and 3% -gelatin.

The samples were kept for at least 3 hours at 18 ° C.

Keeping up the solution at elevated temperature and slow gel formation promotes more stable cross-links [8; 9]. The process of gelatinization in water jellies of gelatin at 20 ° C for 75… 85% takes place after 24 hours [10; 11]. Therefore, the jelly formation of the samples was carried out under the same conditions at a temperature of 18 ° C for 24 hours.

Experimental data on the study of the influence of organic acid salts on the jelly strength of the agar, furcellaran and agaroid are presented in Fig. 2.1… 2.3.

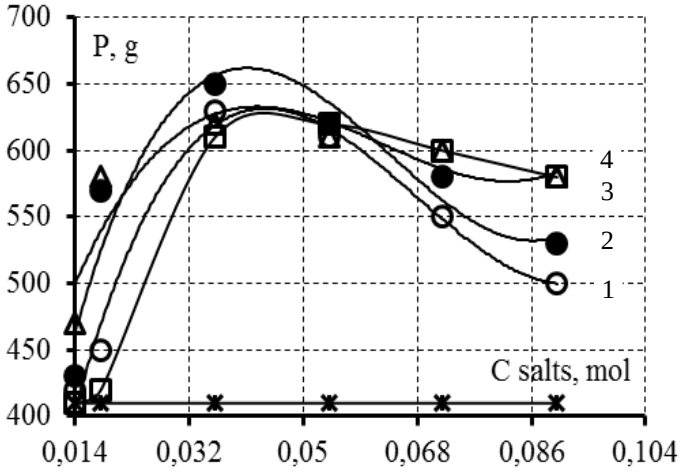

Figure 2.1 - Dependence of strength 4% jelly of agaroid on the concentration of additives: 1- sodium lactate; 2 - sodium acetate; 3 - sodium citrate; 4 - sodium diphosphate; 5 - without additives

The graphs show that the effect of salts on the jelly strength of sulfited polysaccharides is different and depends on the functional properties of the jelly formation agent, the added salt concentration, the nature of the acid.

The structure of the samples is strengthened with the introduction of organic acid salts for agaroid jelly at a concentration of 0.027… 0.054M, for furcellaran - 0.018… 0.056M and for agar - 0.0045… 0.013M.

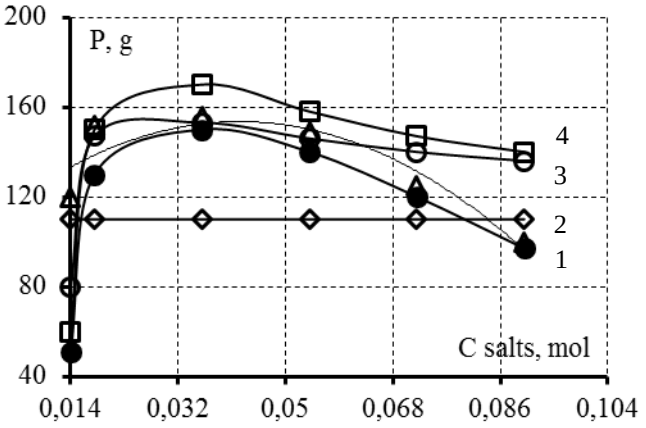

Figure 2.2 - Dependence of strength 2% jelly of furcellaran on the concentration of additives: 1- sodium diphosphate; 2 - sodium acetate; 3 - sodium citrate; 4 - sodium lactate; 5 - without additives

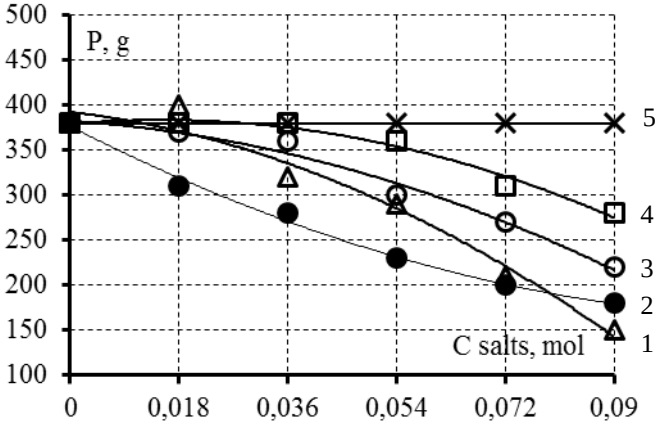

Figure 2.3 - Dependence of strength 2% jelly of agar on the concentration of additives: 1- sodium lactate; 2 - sodium citrate; 3 - sodium acetate; 4 - sodium diphosphate; 5 - without additives

The presence of sodium citrate and sodium lactate to a greater extent strengthens the jelly of gelatin as compared to sodium acetate or sodium diphosphate (Fig. 2.4).

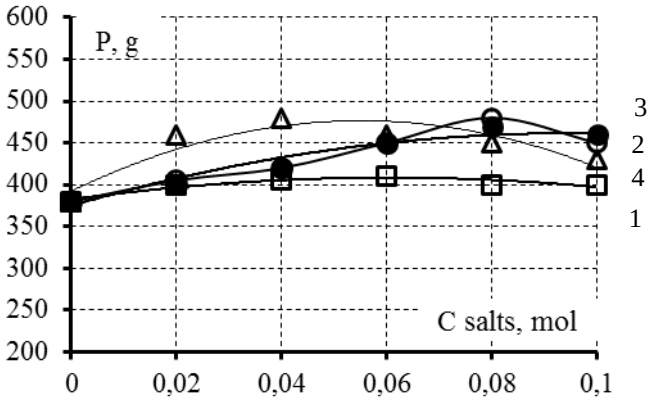

Figure 2.4 - Dependence of strength 3% jelly of gelatin on the concentration of the introduced salts: 1- sodium acetate; 2 - sodium lactate; 3 - sodium citrate; 4 - sodium diphosphate; 5 - without additives

Further increase in the concentration of additives leads to a decrease in strength, apparently due to salting out [12].Thus, at a concentration of 0.009 ... 0.018M sodium citrate reaches a maximum strength of 509 g. The average increase in strength is 30.5% (Fig. 2.5).

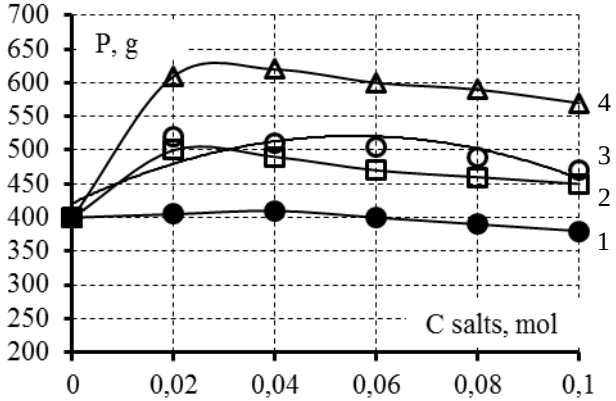

Figure 2.5 - Effect of glycerol concentration on the strength 3% jelly of gelatin with different additives: 1- 0,03M; 2 - 0.08M sodium lactate; 3 - 0.013M sodium citrate; 4 - 0.03M glycerol, 0.08M sodium lactate, 0.013M sodium citrate

Addition of sodium lactate to gelatin contributes to a gradual increase in strength over the range of test concentrations. Jellies, which containing lactic sodium are weaker compared to jellies containing sodium citrate. The strength extremum for the marked sample is in the salt concentration range from 0.07 to 0.09M. The strength at the same time is 470 g, which corresponds to 120.5% relative to the control sample.

The combined presence of the sodium salts of lactate and citrate significantly increase the structural action of gelatin. The strength reaches 589 g or 151% with respect to the strength of the gelatin jelly without additives (Table 2.1).

Table 2.1 – Effect of alcohols and salts on the strength 3% jelly of gelatin

Average value of rational concentrations of alcohols and salts, M							Strength, g
ethyl	glycerol	xylitol	sorbitol	mannitol	sodium salts		
					actate	citrate	
0.00	0.00	0.00	0.00	0.00	0.00	0.00	390
0.00	0.00	0.00	0.00	0.00	0.08	0.00	470
0.00	0.00	0.00	0.00	0.00	0.00	0.013	509
0.00	0.00	0.00	0.00	0.00	0.08	0.013	589
0.03	0.00	0.00	0.00	0.00	0.00	0.00	429
0.03	0.00	0.00	0.00	0.00	0.08	0.00	515
0.03	0.00	0.00	0.00	0.00	0.00	0.013	545
0.03	0.00	0.00	0.00	0.00	0.08	0.013	632
0.00	0.03	0.00	0.00	0.00	0.08	0.00	509
0.00	0.03	0.00	0.00	0.00	0.00	0.013	548
0.00	0.03	0.00	0.00	0.00	0.08	0.013	628
0.00	0.00	0.03	0.00	0.00	0.08	0.00	521
0.00	0.00	0.03	0.00	0.00	0.00	0.013	540
0.00	0.00	0.03	0.00	0.00	0.08	0.013	541
0.00	0.00	0.00	0.03	0.00	0.08	0.013	500
0.00	0.00	0.00	0.03	0.00	0.00	0.013	557
0.00	0.00	0.00	0.03	0.00	0,08	0.013	630
0.00	0.00	0.00	0.00	0.03	0,08	0.00	489
0.00	0.00	0.00	0.00	0.03	0.00	0.013	550
0.00	0.00	0.00	0.00	0.03	0.08	0.013	629

The magnitude of 589 g or 151% is the amount of strengthening afforded by sodium lactate (470 g or 120.5%) and sodium citrate (509 g or 130.5%) combined.

In the literature there is information about the action of strength of alcohols on the structure of jelly [13, 14]. Moreover, the increase in the strength of the structure is observed at significant concentrations of alcohols above 10%. The values of Tables 2.2… 2.5 confirm this data. Thus were investigated representatives of the class of alcohols having different amounts of hydroxyl groups and the value of the hydrocarbon radical.

Table 2.2 - Strength of jelly of agaroid in the presence of alcohols and sodium lactate

Name of alcohols	The strength of 4% agaroid gels, g, with the introduction of alcohol concentration, M / lactate sodium concentration of 0.040 M								
	0.000	**0.0054**	**0.011**	**0.0165**	**0.022**	**0.033**	**0.044**	**0.054**	**0.066**
ethyl	430/ 625	430/ 631	432/ 640	435/ 638	440/ 643	452/ 680	450/ 675	454/ 684	451/ 681
propyl	430/ 618	428/ 634	431/ 635	437/ 650	439/ 642	450/ 682	447/ 681	449/ 673	454/ 669
butyl	430 /619	434/ 638	430/ 640	436/ 641	435/ 649	454/ 676	451/ 684	450/ 671	453/ 677
glycerol	430/6 29	433/ 637	434/ 639	439/ 640	447/ 647	453/ 684	451/ 680	452/ 681	449/ 673
xylitol	430/6 30	430/ 641	431/ 640	434/ 639	437/ 649	457/ 678	450/ 674	449/ 675	439/ 679
sorbitol	430/6 17	431/ 640	433/ 632	432/ 641	458/ 647	452/ 675	459/ 680	447/ 681	451/ 677
mannitol	430/6 19	431/ 633	437/ 637	434/ 639	436/ 641	448/ 679	451/ 677	450/ 684	452/ 678

Table 2.3 - Strength of jelly of furcellaran in the presence of alcohols and sodium lactate

Name of alcohols	The strength of 2% furcellaran gels, g, with the introduction of alcohol concentration, M / lactate sodium concentration of 0.027 M								
	0.000	0.0054	0.011	0.0165	0.022	0.033	0.044	0.054	0.066
ethyl	115/ 154	114/ 155	117/ 159	120/ 162	127/ 176	126/ 174	120/ 160	117/ 161	114/ 157
propyl	115/ 158	115/ 151	116/ 161	119/ 159	126/ 170	129/ 175	121/ 154	119/ 163	115/ 152
butyl	115/ 154	113/ 156	116/ 161	121/ 172	128/ 176	122/ 175	119/ 167	118/ 165	114/ 154
glycerol	115/ 155	116/ 153	117/ 162	120/ 163	124/ 171	127/ 170	122/ 166	117/ 165	116/ 153
xylitol	115/ 151	118/ 157	119/ 160	121/ 164	127/ 177	125/ 174	118/ 163	116/ 166	113/ 155
sorbitol	115/ 157	116/ 154	114/ 162	118/ 160	121/ 174	122/ 175	120/ 164	118/ 162	119/ 155
mannitol	115/ 153	115/ 156	117/ 161	123/ 163	129/ 175	128/ 175	121/ 167	119/ 166	111/ 157

Table 2.4 - Strength of jelly of agar in the presence of alcohols and sodium lactate

Name of alcohols	The strength of 1% agar gels, g, with the introduction of alcohol concentration, M / lactate sodium concentration of 0.009 M								
	0.000	0.0054	0.011	0.0165	0.022	0.033	0.044	0.054	0.066
ethyl	375/ 405	387/ 405	442/ 427	454/ 461	463/ 490	487/ 517	738/ 471	403/ 439	382/ 420
propyl	375/ 402	384/403	440/ 418	453/449	462/ 487	483/ 512	442/ 465	402/ 440	383/ 418
butyl	375/ 404	371/ 407	333/ 429	452/ 461	467/ 497	484/ 519	442/ 451	404/ 440	390/ 415
glycerol	375/ 409	388/ 404	434/ 430	456/ 455	463/ 489	480/ 515	448/ 472	403/ 439	382/ 412
xylitol	375/ 407	387/ 408	449/ 440	451/ 470	460/ 496	481/ 518	442/ 488	398/ 454	380/ 421
sorbitol	375/ 405	388/ 403	444/ 439	455/ 451	463/ 462	488/ 520	443/ 491	397/ 450	379/ 417
mannitol	375/ 405	382/ 409	442/ 441	454/ 459	458/ 478	489/ 507	444/ 485	399/ 451	381/ 417

As can be seen from the tables, the introduction of propyl and butyl alcohols of the same polarity and with a different amount of hydrocarbon radical are not change the jelly-forming ability of the structure-forming agents in comparison with other alcohols. The strength of the samples also remains unchanged when one-, two-, and polyatomic alcohols are added.

The study of the influence of alcohols on the strength jelly of gelatin (Table 2.5) showed that their addition to gelatin does not make any special adjustments in structuring action. Strength thus increases by only 10%. This figure does not depend on the number of hydroxyl groups of polyatomic alcohols and the data obtained in the presence of ethyl alcohol, glycerol, xylitol, sorbitol and mannitol are on average 429 g, and the deviation of the obtained values from the average is within the error of the experiment.

Table 2.5 - Influence of alcohols on the strength of 3% gelatin gels

Alcohols that are introduced, M					Strength, g
ethyl	**glycerol**	**xylitol**	**sorbitol**	**mannitol**	
1	2	3	4	5	6
0.00	0.00	0.00	0.00	0.00	390
0.01	0.00	0.00	0.00	0.00	396
0.02	0.00	0.00	0.00	0.00	425
0.04	0.00	0.00	0.00	0.00	436
0.06	0.00	0.00	0.00	0.00	491
0.08	0.00	0.00	0.00	0.00	384
0.00	0.01	0.00	0.00	0.00	398
0.00	0.02	0.00	0.00	0.00	426
0.00	0.04	0.00	0.00	0.00	422
0.00	0.06	0.00	0.00	0.00	389
0.00	0,08	0.00	0.00	0.00	377
0.00	0.00	0.01	0.00	0.00	399
0.00	0.00	0.02	0.00	0.00	441
0.00	0.00	0.04	0.00	0.00	430
0.00	0.00	0.06	0.00	0.00	400

Continuation of Table 2.5

1	2	3	4	5	6
0.00	0.00	0.08	0.00	0.00	390
0.00	0.00	0.00	0.01	0.00	399
0.00	0.00	0.00	0.02	0.00	438
0.00	0.00	0.00	0.04	0.00	430
0.00	0.00	0.00	0.06	0.00	406
0.00	0.00	0.00	0.08	0.00	392
0.00	0.00	0.00	0.00	0.01	395
0.00	0.00	0.00	0.00	0.02	448
0.00	0.00	0.00	0.00	0.04	426
0.00	0.00	0.00	0.00	0.06	406
0.00	0.00	0.00	0.00	0.08	378

Of greatest interest are studies of the influence of organic acids salts and polyhydric alcohols, the use of which is allowed on food enterprises, on the strength characteristics of the formed jelly. To obtain comparative results in the agar was added organic acids salts. The experimental data are shown in Fig. 2.5… 2.13.

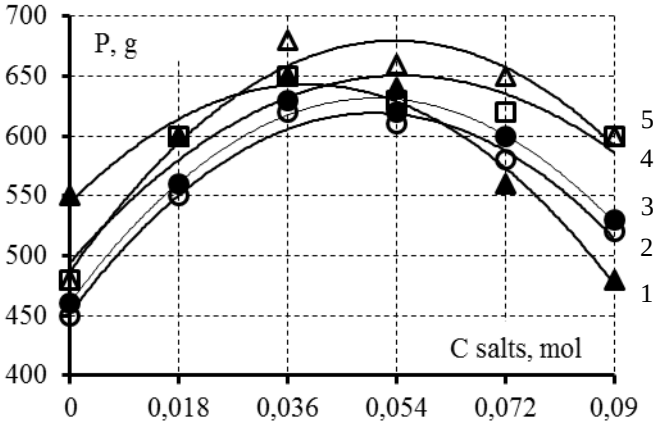

Figure 2.6 - Dependence of the strength of 4% jellies of agaroid on the amount of sodium citrate in the presence of alcohols with a concentration of 0.044M: 1- glycerol; 2 - xylitol; 3 - sorbitol; 4 - mannitol; 5 - ethanol

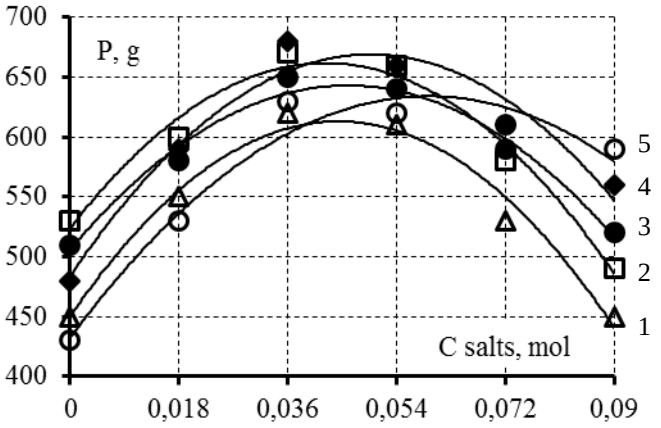

Figure 2.7 - Dependence of the strength of 4% jellies of agaroid on the amount of sodium acetate in the presence of alcohols with a concentration of 0.044M: 1- mannitol; 2 - xylitol; 3 - glycerol; 4 -sorbitol; 5 - ethanol

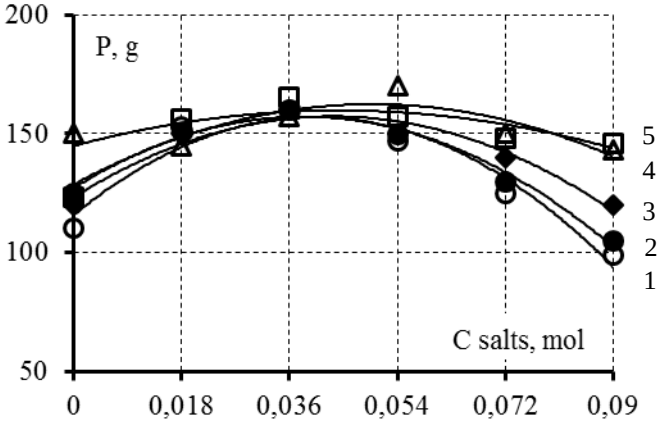

Figure 2.8 - Dependence of the strength of 2% jellies of furcellaran on the amount of sodium lactate in the presence of alcohols with a concentration of 0.044M: 1- glycerol; 2 - sorbitol; 3 - xylitol; 4 - mannitol; 5 - ethanol

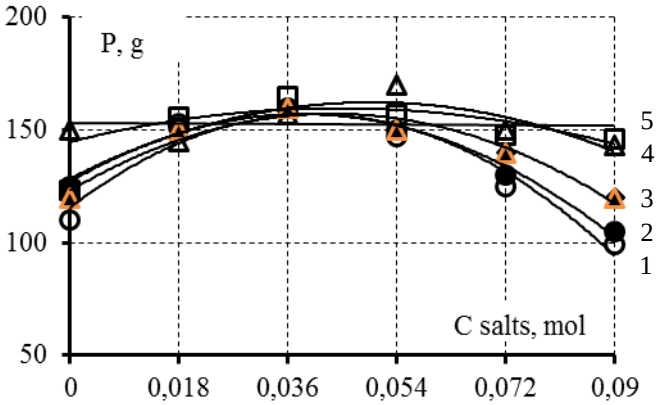

Figure 2.9 - Dependence of the strength of 2% jellies of furcellaran on the amount of sodium citrate in the presence of alcohols with a concentration of 0.044M: 1- ethanol; 2 - mannitol; 3 - glycerol; 4 - sorbitol; 5 - xylitol

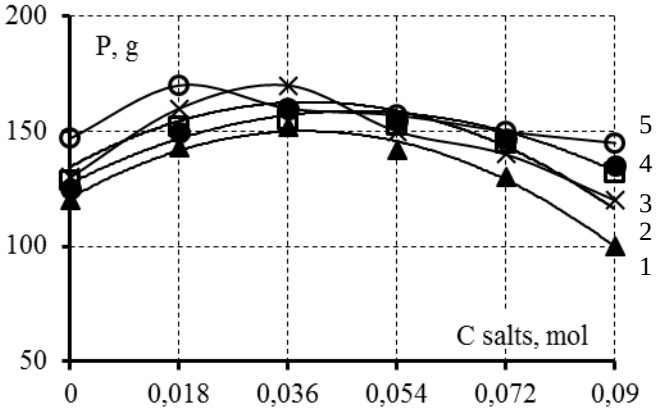

Figure 2.10 - Dependence of the strength of 2% jellies of furcellaran on the amount of sodium acetate in the presence of alcohols with a concentration of 0.044M: 1- glycerol; 2 - xylitol; 3 - sorbitol; 4 -mannitol; 5 - ethanol

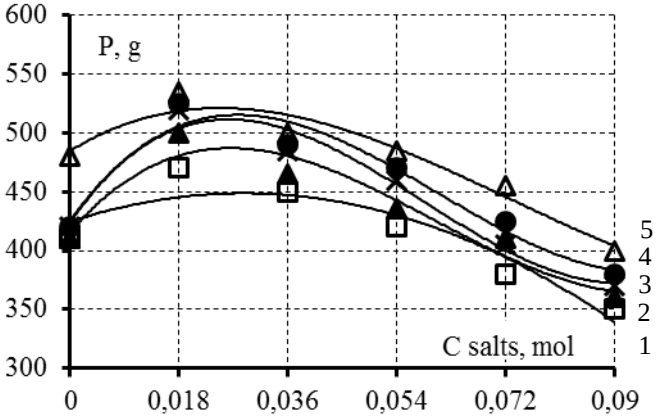

Figure 2.11 - Dependence of the strength of 1% jellies of agar on the amount of sodium acetate in the presence of alcohols with a concentration of 0,033M: 1- mannitol; 2 - glycerol; 3 - sorbitol; 4 - xylitol; 5 - ethanol

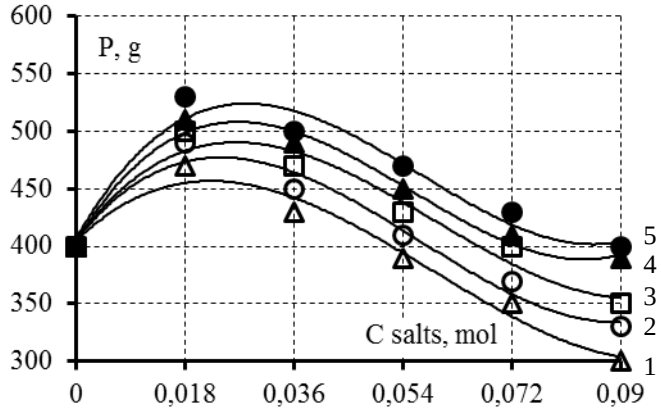

Figure 2.12 - Dependence of the strength of 1% jellies of agar on the amount of sodium citrate in the presence of alcohols with a concentration of 0,033M: 1- xylitol; 2 - glycerol; 3 - sorbitol; 4 - mannitol 5 – ethanol

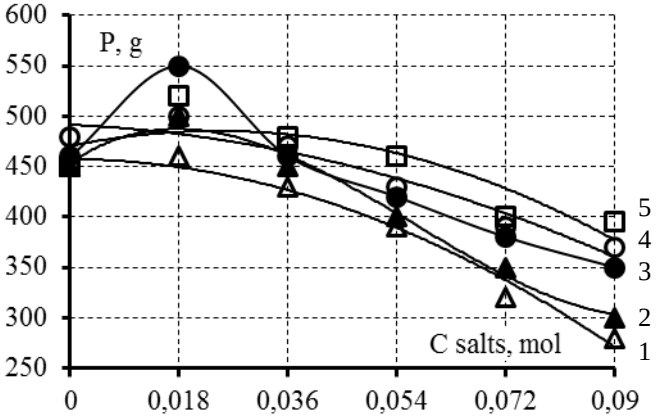

Figure 2.13 - Dependence of the strength of 1% jellies of agar on the amount of sodium lactate in the presence of alcohols with a concentration of 0,033M: 1- sorbitol; 2 - xylitol; 3 - glycerol; 4 - mannitol 5 – ethanol

Analysis of the presented graphical dependencies shows that the jelly strength of agaroid, furcellaran and agar with the addition of salts and alcohols is much higher than in samples containing only OAS. This structuring effect of "alcohol-salt sensuality" persists regardless of the nature of salt and alcohol.

The jelly of agaroid with the addition of OAS are increased by 45% , furcellaran - 35%, agar - 8%, and with the introduction of PAA, respectively, by 5, 12, 30%. The joint presence of OAS and PAA increases the strength in the jelly of agaroid by 58%, furcellaran - 53%, agaroid - 38%. Moreover, these 58% increase in strength for jelly of agaroid do not correspond to the total amount. Due to the addition of OAS, the jelly-forming ability increases by 45%, due to the PAA - 5% and 8% is brought to joint action, and in the structure of furcellaran it is 6%, in the agar jelly - 0%.

The highest strength of gelatin jelly occurs at the concentration of alcohol of 0.02… 0.04, sodium lactate - 0.07… 0.09 M and sodium citrate - 0.009… 0.018 M. Structural effect of "alcohol-salt sensuality" of gelatin, as well as sulfited

polysaccharides, is observed only when organic acid salts are added together with polyatomic alcohols. The strength is 628 g or 161% compared to the gelatin jelly without modifying additives. The marked strengthening of the structure is equal to the sum of the increments in the strength of the jelly, which is obtained as a result of the introduction of each ingredient (Table 2.1, Fig. 2.3, 2.4).

Thus, in order to maximize the structure of the jelly of the agaroid, it is necessary to add organic acids salts together with polyatomic alcohols in the amount of 0.027… 0.054 M and 0.033… 0.066M, respectively, furcellaran - 0.018… 0.036 M and 0.033… 0.044M, agar - 0.0045… 0.013M and 0.027… 0.039M, gelatin - 0.07… 0.09M (0.8… 1.0%) - sodium lactate and 0.009… 0.018M (0.2… 0.4%) - sodium citrate, 0 , 02… 0,04M - polyatomic alcohol.

2.1.2 Influence of polyatomic alcohols and salts on the jelly strength of sulfited spolysaccharides

In addition to the sodium salts of organic acids, the influence of Fe (III) ions (as a 50% solution of six hydrogen chlorine iron) was studied as a modifying additive on the strength properties of jelly of agaroid, furcellaran and agar. The trivalent iron ions were introduced into the polysaccharide solution cooled to 70 ° C, as the destruction of macromolecules was observed at higher temperatures [15] and the strength of the samples decreased sharply. The research data are presented in Table 2.6.

Table 2.6 - Influence of Fe (III) ions on the strength properties of gels of of red seaweed polysaccharides

Agaroid 4.0% concentration					**Furcellaran 2.0% concentration**					**Agar 1.0% concentration**				
concentration of additives					**concentration of additives**					**concentration of additives**				
$FeCl_3 \times 6H_2O$ M %		Glycerol M %		strength, g	$FeCl_3 \times 6H_2O$ M %		glycerol M %		strength, g	$FeCl_3 \times 6H_2O$ M %		glycerol M %		strength, g
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.00	0.00			430	0.00	0.00			115	0.00	0.00			375
0.0045	0,12			510	0.0045	0.12			128	0.045	0.012			380
0.007	0,18			574	0.007	0.18			136	0.007	0.18			382
0.009	0,23			623	0.009	0.23			162	0.009	0.23			376

Continuation of Table 2.6

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.018	0,46			651	0.018	0.46			153	0.018	0.46			358
0.027	0,69			622	0.027	0.69			142	0.027	0.69			312
0.36	0,92			267	0.036	0.92			121	0.036	0.92			218
0.018	0,46	0,022	0,2	650	0.009	0.23	0,022	0,2	212	0.0015	0.12	0.022	0.2	489
0.018	0,46	0,044	0,4	884	0.009	0.23	0,044	0,4	182	0.0046	0.12	0.044	0.4	396
0.018	0,46	0,065	0,6	734	0.009	0.23	0,065	0,6	159	0.0045	0.12	0.65	0.6	378
0.018	0,48	0,087	0,8	519	0.009	0.23	0,087	0,8	138	0.0045	0.12	0.87	0.8	375

The table shows that with increasing concentration of $FeCl_3 \times 6H_2O$ in agaroid there is a strengthening of the jelly and the highest value (651 g) is obtained at an additive concentration in the range 0.009… 0.027 M, in furcellaran - 0.007… 0.018M and in agar - 0.0045… 0 , 0078M.

With the combined presence of iron chloride and glycerol, agaroid jelly is enhanced to a greater extent. In this case, P = 884 g, and the alcohol concentration is 0.044 ... 0.065 M, for furcellaran - 0.022 ... 0.044 M and agar - 0.022 ... 0.039 M.

Thus, to increase the strength of the jelly of sulfited polysaccharides it is necessary to add chlorine iron and polyatomic alcohol. In this case, the cost of modifying additives for the agarid is maximum and for the agar is minimal.

A practical and theoretical interest is the study of the influence of the surface layer on the mechanical strength of the jelly. The results of the experiments on the study of the jelly strength of the agaroid with naturally formed (NF) and with a cut surface layer are presented in table. 2.7. The samples were kept at 180 × 60 s at 18 ° C.

The presence of the polyvalent Fe III ion (in the form of chlorine iron) in the jelly of agaroid makes significant adjustments. With six free orbitals, iron is an acceptor of unpaired electronegative atoms of 0, S, and other entering to atomic groups of macromolecules of the jelly formation agent. By forming associates of these macromolecules, iron reduces their mobility, slows down confirmatory transformations, promotes the formation of spatial structures throughout the volume, and impedes the free accumulation of molecules on the surface. This increases the strength of the jelly and reduces the surface effect [16].

Table 2.7 - Influence of the surface layer on the mechanical strength of the jelly of the agaroid

Composition of jelly	The concentration of additives, mol	Strength of 4% jelly of agaroid, g					
		NF	Cut	ΔP	with the additive of 0,02% Fe		
					NF	Cut	ΔP
Agaroid	-	440	340	23	500	400	20
Agaroid+ sodium lactate	0.09	475	365	23	760	720	5
Agaroid+ glycerol	0.11	270	215	20	760	685	10
Agaroid+ sodium lactate + glycerol	0.09 0.11	740	590	20	740	735	1

where ΔP – is the relative strength reduction, %

Removal of the naturally formed surface layer of the jelly of agar with various additives leads to a decrease in strength within 20 ... 23%.

The surface tension of water in the presence of agaroid and various additives decreases over time. A steady-state value can only be obtained in a few hours. This indicates the slow confirmatory transformation of macromolecules in the surface layer, which try to occupy an energy-favorable position at the interface between the liquid and gaseous phases. The higher the temperature (ie, the more mobile the atomic groups), the faster the accumulation of molecules in the surface layers and the confirmatory transformations will occur. For 4% jelly of agaroid, this interval ranges from 40 ° C to the temperature of the jelly formation. Thus, the confirmatory transformations in the surface layer and the influence of the surface on the strength of the jelly should be more noticeable if the solution of the gelling agent is maintained before solidifying at a relatively elevated temperature.

To this end, the strength of agaroid jelly without and in the presence of chlorine iron was studied, the results of which are shown in Table 2.8.

Table 2.8 - Influence of solidification regimes of agaroid solutions on the strength of the formed gels

Composition of jelly	Strength, g		Relative strength changes P %
	A	B	
4.0 % agaroid	400	468	17
4.0 % agaroid +0.02% Fe	740	765	4

where A and B – solidification conditions:
A – 3 h at t=19°C;
B – 3 h at t=35°C and 3 h at t=19°

The table shows that the agaroid solution, which was kept at 35 ° C had conditions more favorable for the confirmatory transformation of macromolecules in the surface layer. Jellies of this solution formed a relatively high strength (P = 17%). Iron III ion, contributing to a significant strengthening of the jelly grid, inhibits the transition of macromolecules into the surface layer, thus reducing the effect of surface influence on the jelly strength [17].

The mutual influence of the two salts in the presence of polyatomic alcohols on the strength properties of the fikokoloids was also studied. Salt concentrations are selected from the most rational ones: in the jelly of agaroid - 0,027 ... 0,054 M, furcellaran - 0,016 ... 0,036 M, agar - 0,0045 ... 0,013 M. The research data are shown in Table 2.9.

Table 2.9 - Jelly strength in the presence of glycerol and in combination with various salts

Name of sodium salts	Strength,% to control samples of 4.0% agaroid, 2.0% furcellaran and 1.0% agar with the addition of: two salts / two salts with glycerol				
	sodium lactate	sodium citrate	sodium acetate	sodium diphosphate	sodium chloride
1	2	3	4	5	6
Jelly of agaroid					
lactate	130/182	256/276	197/217	201/206	215/223
citrate	256/276	185/203	294/313	323/324	293/307
acetate	197/217	294/313	147/167	213/222	308/302

Continuation of Table 2.9

1	2	3	4	5	6
diphosphate	201/206	323/324	213/222	125/176	216/231
chloride	215/223	293/307	308/302	216/232	218/241
Jelly of furcellaran					
lactate	136/148	184/202	196/207	121/118	224/282
citrate	164/202	207/220	233/236	247/256	251/285
acetate	196/207	233/236	169/183	152/156	211/278
diphosphate	121/118	247/256	152/156	94/99	92/144
chloride	224/282	251/345	211/278	92/144	178/187
Jelly of agar					
lactate	109/112	107/143	106/118	108/109	106/118
citrate	110/116	110/147	111/121	114/117	107/122
acetate	105/124	108/131	107/119	106/109	108/116
diphosphate	103/107	105/109	104/105	98/106	103/106
chloride	97/115	99/111	95/108	94/113	93/126

It should be noted that "alcohol-salt sensuality" depends on the content of sulfites in the polysaccharides and the nature of the salts added.

The obtained results allow us to conclude that the increase in jelly strength corresponds to a decrease in the surface tension of the solutions. The introduction of chlorine iron makes significant adjustments to the process of the confirmatory transformation of macromolecules in the surface layer, which try to occupy a more energy-favorable position at the interface between the liquid and gaseous phases, depending on the temperature of the structure. The strength of the jelly with the combined introduction of the two salts is higher than the addition of each salt separately. An exception is sodium diphosphate, which has an inhibitory effect on increasing the strength of the jelly of furcellaran and agar with the addition of sodium salts.

The presence of alcohol in such systems (with two salts) has the ability to further enhance the mechanical strength of the jelly. Thus, the strength of a 4% jelly of agaroid with the addition of sodium chloride and sodium lactate is 215% relative to the control sample, and in the presence of glycerol, this figure increases to 223%.

The strengthening of the jelly occurs to varying degrees depending on the type of salt added. The most successful are combinations of different ingredients. Particularly for jelly of agaroid with sodium citrate, and also with sodium chloride for furcellaran - with sodium lactate, sodium citrate and sodium chloride, for agar - with sodium citrate and sodium acetate.

2.1.3 Investigation of structural and mechanical characteristics of jelly

Jelly of agaroid, furcellaran, agar and gelatin in their inherently elastic-plastic-viscous and strength parameters occupy an intermediate position between perfectly-elastic and perfectly-viscous bodies. The presence of an internal structure gives them certain mechanical properties - springiness, elasticity, plasticity, viscosity, strength, which objectively characterize their consistency and depend on the nature of the substances that enter the system and the forces of interaction between them.

The jelly under consideration has a complex crystallization-coagulation structure. The crystallization structure is determined by double molecular helices, and in particular by their aggregates, in the molecular grid of jelly , and coagulations by the interaction of unspiralized areas of polysaccharide macromolecules between double molecular helices and their aggregates [28].

The jelly of agarids, furcellaran, agar, which in their structure have a considerable number of aggregates of molecular spirals, exhibits more springy-elastic properties. Plastic-viscous properties are poorly developed and, as a result of exceeding the maximum shear stress, the system usually collapses.

The presence of lactic acid sodium salt in the system contributes to the increase of springy properties while reducing plasticity and elasticity (Table 2.10).

Table 2.10 - Rheological characteristics of agaroid jelly in the presence of OAS and PAA

Concentration of additives, M		Deformation, 10^{-4}, M			Plasticity, %	Springiness, %	Elasticity, %
SL	Gl	ε_o	ε_{ins}	ε_{res}			
0.00	0.00	2.59	4.43	1.49	33.7	58.5	41.5
0.036	0.00	2.94	3.74	1.22	32.6	78.5	21.5
0.09	0.00	2.87	3.30	0.60	18.1	86.8	13.2
0.36	0.00	2.61	2.94	0.53	17.9	89.0	10.9
0.00	0.044	2.09	4.31	1.66	38.5	48.5	44.7
0.00	0.11	2.11	5.30	2.16	40.7	39.8	60.2
0.00	0.44	2.43	6.06	2.87	47.3	40.2	59.8
0.036	0.044	1.97	4.54	2.02	44.5	43.4	56.5
0.09	0.011	2.39	4.61	2.02	47.8	51.7	48.3
0.36	0.44	2.91	4.66	2.26	48.5	62.5	37.6

If the jelly structure is stabilized, mainly by nodes of double molecular helices, then the springy-plastic-viscous properties are shown. Since glycerol in the system increases the plasticity of the system, it can be assumed that alcohol (as well as sugar) is able to inhibit the aggregation of macromolecule helices [28, 29].

Comparison of the structural and mechanical characteristics of the agaroid jelly with the introduction of glycerol and sodium lactate with similar indicators of the control sample shows that the additives increase the plastic and elastic properties of the jelly, reducing its springiness. Structures with additives are characterized by a plasticity equal to 44.5%, springiness - 43.3% and elasticity - 56.5%, and in the control sample marked indicators are respectively 33.7%, 59.5% and 41.5%.

Increasing the concentration of modifying additives to 4% of each leads to a further increase in the plasticity of the system. If in the control sample P = 33.7%, then in the marked sample P = 44.5%. The springiness increases from 43.4% to 62.5%, which is slightly higher than in the control sample - 58.5%. In this case, the elasticity changes in the opposite order - decreasing from 56.5% to 37.6%, ie below control - 41.2%.

The fact that the structure of the jelly with additives is less plump and denser than the original sample, explains the increase in their mechanical strength.

The introduction of chlorine iron into polysaccharide solutions leads to an increase in springiness and a decrease in the elasticity of their jelly. This is probably due to the fact that iron ions are able to form intermolecular bonds of ionic type that bind polymer chains [29]. The formation of such bonds increases the rigidity of the polymer chains, resulting in a decrease in elasticity and an increase in the springiness of the jelly. The plasticity of the system is reduced (Table 2.11).

Table 2.11 - Rheological characteristics of jelly of sulfited polysaccharides in the presence of Na КМЦ and $FeCl_3$

Name of jelly forming agents and concentration of additives, M	Deformation, 10^{-4}, M			Plasticity, %	Springiness, %	Elasticity, %
	ε_o	ε_{ins}	ε_{res}			
1.0% agar	3.78	4.75	1.63	35.5	79.9	20.1
1% agar +0.1% Na CMC	3.82	5.02	3.11	62.0	76.1	23.9
1.0% agar +0.3% $FeCl_3$	3.90	4.33	1.47	33.9	90.0	10.0
1.0% agar +0.1% Na CMC+0.03% $FeCl_3$	3.86	4.49	2.26	50.3	86.0	14.0
2.0% furcellaran	8.81	14.21	4.59	32.3	69.0	31.0
1% furcellaran +0.1% Na CMC	10.01	15.40	7.77	50.5	65.0	35.0
1.0% furcellaran +0.3% $FeCl_3$	10.28	12.95	3.90	30.1	79.4	20.6
1.0% furcellaran +0.1% Na CMC+0.03% $FeCl_3$	9.90	30.20	5.31	40.2	75.0	25.0
4.0% agaroid	2.74	4.29	2.75	17.5	63.9	36.1
1.0% agaroid +0.1% Na CMC	2.81	4.70	1.90	40.4	59.8	40.2
1.0% agaroid +0.3% $FeCl_3$	2.70	3.41	0.51	15.0	79.2	20.8
1.0% agaroid + 0.1% Na CMC+0.03% $FeCl_3$	2.92	4.23	1.30	30.7	69.0	31.0

The addition of sodium carboxymethyl cellulose leads to a significant increase in the plasticity of the jelly.

Co-administration of Na CMC and $FeCl_3$ increases both springiness and plasticity of the system, but the elasticity is reduced. The plasticity of the 3% gelatin jelly is 40.0%, with the addition of 0.022M glycerol - 41.3% and 0.44 M - 42.9%. The presence of alcohol in the jelly helps to increase plasticity (Table 2.12).

Table 2.12 - Structural and mechanical characteristics of 3% gelatin jelly in the presence of modified additives

Concentration of additives, M			Deformation, 10^{-4}, M			Plasticity, %	Springiness, %	Elasticity, %
Gl	SL	SC	ε_o	ε_{ins}	ε_{res}			
0.00	0.00	0.00	3.40	4.00	1.60	40.0	85.0	15.0
0.022	0.00	0.00	6.90	8.00	3.50	41.3	86.3	13.8
0.44	0.00	0.00	7.50	9.20	3.90	42.9	85.8	14.0
0.00	0.072	0.00	5.60	6.50	2.60	39.7	86.1	13.8
0.00	0.18	0.00	7.90	9.06	3.60	39.7	87.2	12.8
0.00	0.00	0.013	8.50	9.49	3.70	38.9	89.6	10.3
0.00	0.00	0.08	8.90	9.80	4.00	40.8	90.8	9.3
0.022	0.072	0.013	7.90	9.05	4.20	46.4	87.2	12.8

The deviation of the springiness and elasticity from the level of the control sample is within the error of the experiment.

The lactic acid sodium salts have little influence on the plasticity of the gelatin jelly. However, both sodium lactate and sodium citrate help to increase springiness and reduce elasticity. An increase in the concentration of OAS in jelly changes the deviation of structural and mechanical characteristics to a greater extent.

The modifying additives that are jointly present in the gelatin jellies significantly alter the structural and mechanical parameters compared to the control sample. The springiness of the jelly containing 0.022M glycerol, 0.072M sodium lactate and 0.013M sodium citrate increases and is 87.2%, the plasticity also increases to 46.4%, while the elasticity decreases to 12.8%.

The mesh structure of the diluted jelly determines their springy properties, and the weak interaction between the sections of the chains - high elasticity and absence of relaxation phenomena.

The increase in the springiness of the grid at low concentrations of organic acid salts probably indicates the formation

of additional bonds. The decrease in elasticity confirms this assumption and may be due to the decrease in the size of vacant areas as a result of the formation of additional connections.

Thus, with the introduction of organic acids salts and polyatomic alcohols, the jelly of polysaccharides along with the springy -elastic properties have plastic-elastic, and with the addition of Na CMC and $FeCl_3$ - plastic. In gelatin jellies, plastic-springy properties predominate.

2.1.4 Study of influence of thermostating process duration and the solutions temperature on the jelly strength of the polysaccharide

A study of the jelly strength of agar, furcellaran and agaroid on the value of temperature and the duration of their thermostating showed that organic acid salts and polyatomic alcohols have a significant impact on changes in the structure of fikokoloids (Tables 2.13…2.15).

Table 2.13 - Dependence of jelly strength of agar on temperature and thermostating duration of solution

Composition of jelly, %	The values of P, g, at t ° C, for τ × 60 s					
	70°C		80°C		90°C	
	30	60	30	60	30	60
1	2	3	4	5	6	7
agar – 1.0	365	356	357	347	345	334
agar – 1.0 sodium lactate – 0.1	368	359	361	352	351	341
agar – 1.0 glycerol – 0.3	371	363	367	356	356	344
agar – 1.0 sodium lactate – 0.1 glycerol – 0.3	373	367	371	361	361	350
agar – 1.0 sodium lactate – 0.1 xylitol – 0.5	370	365	370	358	361	347
agar – 1.0 sodium lactate – 0.1 sorbitol – 0.6	374	367	370	358	361	346

Continuation of Table 2.13

1	2	3	4	5	6	7
agar – 1.0 sodium lactate – 0.1 mannitol – 0.6	372	366	371	359	358	351
agar – 1.0 citric acid – 1.0	359	309	293	260	291	221
agar – 1.0 sodium lactate – 0.1 glycerol – 0.3 citric acid – 1.0	366	361	365	656	352	344

Table 2.14 - Dependence of jelly strength of furcellaran on temperature and thermostating duration of solution

Composition of jelly, %	**The values of P, g, at t ° C, for τ × 60 s**					
	70°C		**80°C**		**90°C**	
	30	**60**	**30**	**60**	**30**	**60**
1	2	3	4	5	6	7
furcellaran – 2.0	96	80	78	60	69	55
furcellaran – 2.0 sodium lactate – 0.3	107	92	89	72	80	67
furcellaran – 2.0 glycerol – 0.35	112	98	96	79	86	78
furcellaran – 2.0 sodium lactate – 0.3 glycerol – 0.35	113	100	99	83	90	78
furcellaran – 2.0 sodium lactate – 0.3	114	99	100	82	91	77
furcellaran – 2.0 sodium lactate – 0.3 sorbitol – 0.7	114	98	99	83	90	79
furcellaran – 2.0 sodium lactate – 0.3 mannitol – 0.7	113	100	98	86	88	81
furcellaran – 2.0 citric acid – 1.0	82	70	69	51	57	41
furcellaran – 2.0 sodium lactate – 0.3 glycerol – 0.35 citric acid – 1.0	108	96	93	75	83	70

Table 2.15 - Dependence of jelly strength of agaroid on temperature and thermostating duration of solution

Composition of jelly, %	The values of P, g, at t ° C, for τ × 60 s					
	70°C		80°C		90°C	
	30	60	30	60	30	60
1	2	3	4	5	6	7
agaroid – 4.0	320	197	240	187	197	157
agaroid – 4.0 sodium lactate – 0,4	349	222	261	209	218	179
agaroid – 4.0 glycerol – 0.4	397	270	309	251	246	227
agaroid – 4.0 sodium lactate – 0.4 glycerol – 0.4	407	306	331	274	269	241
agaroid – 4.0 sodium lactate – 0.4 xylitol – 0.67	405	300	337	270	260	249
agaroid – 4.0 sodium lactate – 0.4 sorbitol – 0.8	400	312	330	280	260	237
agaroid – 4.0 sodium lactate – 0.4 mannitol – 0.8	402	298	331	275	251	232
agaroid – 4.0 citric acid – 1.0	105	76	101	69	62	37
agaroid – 4.0 sodium lactate – 0.4 glycerol – 0.4 citric acid – 1.0	375	251	280	230	231	199

As the duration of heating increases, the jelly strength decreases, thus increasing the storage temperature. The introduction of sodium lactate helps to reduce the negative effects of heat treatment.

Organic acid salts at concentrations above 0.5% do not improve the structure of the jelly and do not increase the resistance of their negative acid action at high temperatures.

The addition of glycerol in the structure forming agent also inhibits the strength of the jelly. Moreover, the presence of alcohols

with different amounts of hydroxyl groups does not change the general trend, which indicates that no influence of the number of hydroxyl groups on this process.

The introduction of organic acids greatly accelerates the hydrolysis of jelly forming agents when they are heat treated. This is more true of agaroid, less so of agar. With increasing acid concentration, jelly strength decreases to a greater extent. The reason is that the decrease in the mechanical strength of the jelly under the influence of organic acids is caused not only by acid hydrolysis, but also by the interaction of the polar groups of the structure-forming agent and the polar groups of added acids, which leads to a weakening of the bonds between the molecules of the jelly forming agent.

The joint introduction of organic acids salts and polyatomic alcohols contributes to a significant inhibition of the hydrolysis process of the jelly forming agent. By performing a protective action, alcohols slow down the rate of fall of the structure, contribute to reducing the cost of the jelly forming agent.

The obtained results allow to state that polyatomic alcohols exert a significant protective effect on the structure-forming agent when they interact with organic acids and high temperature, especially it is manifested in the joint alcohol-salt presence in the jelly.

2.1.5 Investigation of the structure formation kinetics

The rate of increase in the strength of the jelly in the formation of the structure depends on the concentration of the structure, its chemical composition and solidification temperature [1, 2].

The cooling of polysaccharide solutions well below the solidification temperature at different speeds does not affect the strength of the formed jelly. Holding formed jelly at a temperature of 1… 2 ° C below the temperature of structure formation before cooling to lower temperatures significantly increases their strength. The strengthening of the jelly is also observed if the solutions during

cooling are holded for some time at constant temperatures at 10… 15 ° C above the freezing point of the system. Similar changes at temperatures below critical in solutions give rise to additional ordering and orientation by joining elements of the structure, as well as forming new bonds, which contributes to the strengthening of the jelly. The lack of effect on the jelly strength of different cooling rates of the solutions can be explained by the same circumstances that, with constant decrease in the temperature of the solutions in the secondary structures, there is a continuous formation of new bonds that impede their ordering.

The increase in the strength of jelly agaroid as a result of their holding at temperatures of 1 ... 2 ° C below solidification temperatures, before subsequent cooling, is explained by the relaxation processes of the stratification of the stress that arose in jelly during their formation, the additional ordering and orientation of the elements of structure and formation connections. The process is easier in un cooled jelly at temperatures close to solidification temperatures. With the quickly cooling of the jelly, the bonds formed at these temperatures interfere with the proper ordering of the structure, and some of the bonds that could form at lower temperatures are not formed. Jelly in this case have reduced strength.

It is of particular interest to study the process of jelly structure forming, depending on the presence of modifying additives. To characterize the dynamics of this process, a study of the strength of systems over time at a constant temperature of 20 ° C was chosen. The presence of modified additives significantly accelerates the process of forming the structure, regardless of the nature of the jelly forming agent (Fig. 3.1… 3.4).

Depending on the chemical composition and nature of the structure-forming agent, the rate of increase in jelly strength varies. Thus, after 30 × 60 s of structure-forming, the jelly strength of 4% agaroid solution is 130 g, while the structure of a 4% jelly with additives has reached 360 g, while the ΔP was 230 g or 277%, for furcellaran and agar, respectively, 80 g or 260%, 250 g or 225% (Fig. 2.14… 2.16, curve 1 and 4).

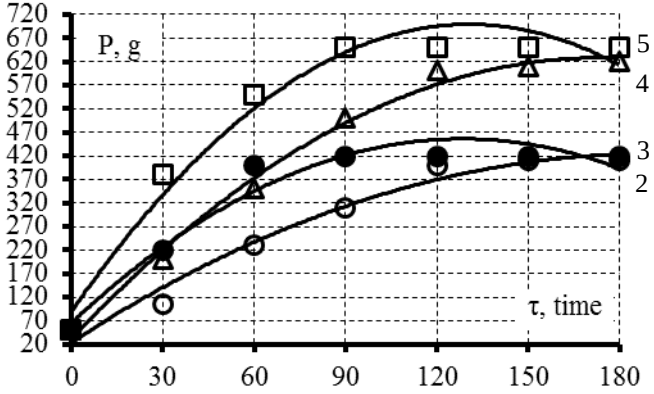

Figure 2.14 - Dependence of the gels strength of agaroids on the duration of structure formation: 1- agaroid 4.0%; 2 - agaroid 4.0%, sodium lactate 0.4%; 3 - agaroid 4.0%, glycerol 0.4%; 4 - agaroid 4.0%, sodium lactate 0.4%, glycerol 0.4%

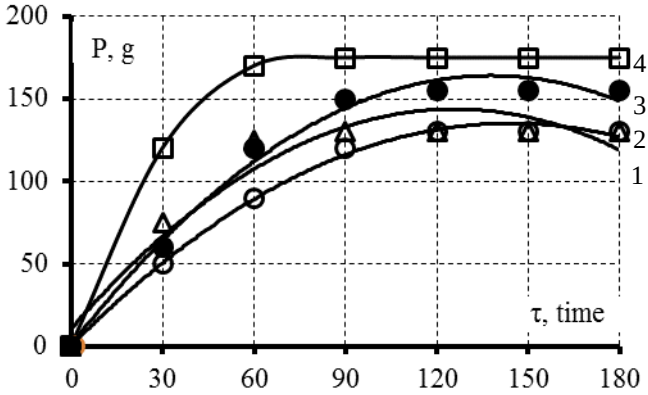

Figure 2.15 - Dependence of the gels strength of furcellaran on the duration of structure formation: 1- furcellaran 2,0%; 2 – furcellaran 2,0%, sodium lactate 0,3%; 3 – furcellaran 2,0%, glycerol 0,35%; 4 – furcellaran 2,0%, sodium lactate 0,3%, glycerol 0,35%

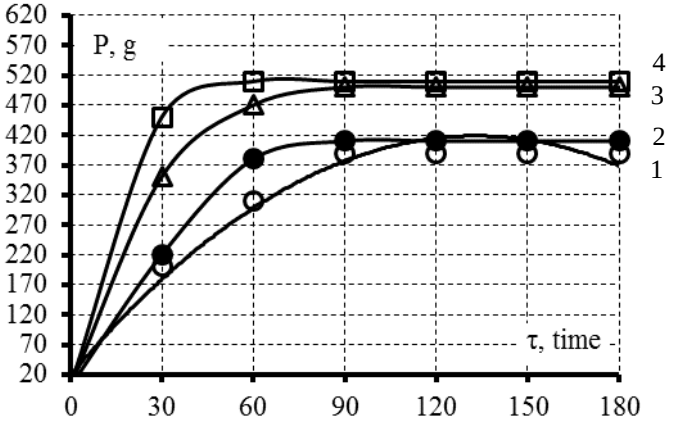

Figure 2.16 - Dependence of the gels strength of agar on the duration of structure formation: 1- agar 1,0%; 2 – agar 1,0%, sodium lactate 0,1%; 3 – agar 1,0%, glycerol 0,3%; 4 – agar 1,0%, sodium lactate 0,1%, glycerol 0,3%

The graph shows that at the end of the marked time, the maximum increase in strength was in the jelly of agaroid, and the minimum - in the agar. A similar tendency of strength change is observed after complete jelly formation of systems. This again proves the feasibility of using modifying additives for a qualitative change in the jelly-forming ability of structure-forming agents.

When studying the kinetics of structure formation of the jelly gelatin instead of strength determined the modulus of springiness, which is associated with a considerable duration of structure formation. However, even after 150 × 60 s, there is a clear difference in the change in the modulus of springiness depending on the additives introduced (Fig. 3.4, curve 1 and 3).

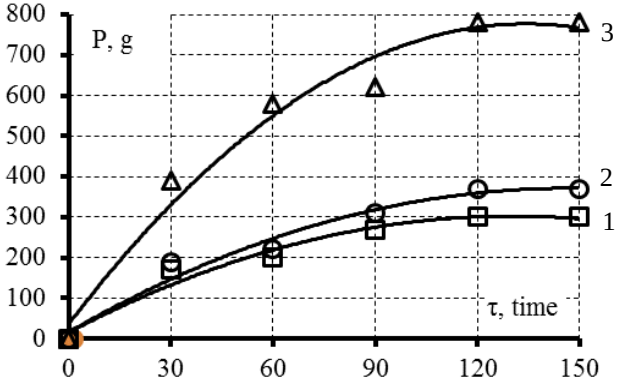

Figure 3.4 - Influence of modifying additives on the kinetics of gel formation of jelly: 1 - 3%: gelatin; 2 - 3% gelatin, 0.8% sodium lactate, 0.2% glycerol; 3 - 2.5% gelatin, 0.8% sodium lactate, 0.3% sodium citrate, 0.2% glycerol

The use of organic acid salts and polyatomic alcohols in the most rational concentrations allows to influence the strength properties of the jelly of the structure-forming agents.

2.1.6 Characterization of physicochemical properties of pectin extracts

Influence of technological parameters on the degree of esterification of pectin during the process of obtaining dry pectin extracts. The structure of a molecule of any pectin has carboxylic groups: free -COOH and methoxylvane - $COOCH_3$. The properties of pectin depend on the proportion of these groups (degree of esterification). Pectins are divided into low-esterificated (LEP) and highly-esterificated (HEP). LEP are used to form complexes with inorganic compounds and they are mostly used for therapeutic-prophylactic purposes, and HEP are used in confectionery industry to form gels. Natural apple pectin belongs to HEP class with degree of methoxylation of 75 ... 78%. The process of demethoxylation that depends on the pH of environment, temperature and duration of drying was investigated on the basis of apple pectin.

The study of this process is based on the method of mathematical planning of an experiment. Box's matrix of optimal scheduling ($B_п$) was used for forming the plan of the second order and creating a quadratic mathematical model (EP) [41]. This method of planning belongs to D-optimal methods (from the word

determinant), the application of which allows obtaining maximum amount of accurate information in the course of a minimum number of experiments. The research was conducted according to the scheme of three-factor experiment with determining the optimal points of the process.

Impact factors were selected:

$$XI = (pH - pH_0)/\Delta pH;\ X2 = (t - t_0)/\Delta t;\ X3 = (\tau - \tau_0)/\Delta\tau \qquad (4.29)$$

pH -environment (concentration of hydrogen ions H^+);

t - temperature of the environment, °C;

τ- duration, s.

Te degree of methoxilation (ξ,%) is considered as a state variable.

Normalization of appropriate factors was conducted using dimensionless variables, the levels of their variation are presented in table. 4.10:

Table 4.10. – Levels of factors of plan B_3

Name	Factors			
	Code	XI	X2	X3
Low level	-1	2.5	104	5
Upper level	+1	3.8	130	18
Zero level	0	3.15	117	11.5
Interv al of variation		0.65	13	6.5

Equations for practical calculations were obtained after confirmation of the adequacy of mathematical model:

$$\xi = 931{,}959 - 240{,}721\cdot pH - 8{,}1904\cdot t - 2{,}9344\cdot x + 0{,}222\cdot pH\cdot t + 0{,}7988\cdot pH\cdot\tau - 0{,}016\cdot x\cdot\tau + 33{,}876\cdot pH^2 + 0{,}0314\cdot t^2 + 0{,}0548\cdot\tau^2. \qquad (4.30)$$

To find the minimum surface response we applied gradient method. The lowest value degree of esterification was obtained at the maximum value of duration (x = 18 s), the minimum value of pH of environment 2.5 and the maximum temperature of 130°C.

Viscosity, density, surface tension of concentrated pectin extracts. Viscosity, density, surface tension of high-concentrated pectin extracts were studied to calculate the technological regimes and technological equipment [49, 52-56].

One of the main characteristic properties of pectin substances as lyophilic colloids is viscosity. It is explained by the fact that pectin molecules easily associate with each other or with large molecules of related substances to form aggregates. The second

reason is excessive hydration of high-polymeric molecules that determines their shape [2].

The viscosity of water solutions of pectin and pectin extracts depends on the temperature, content of solids, content of pectin substances and the nature of pectins (degree of esterification and polymerization, molecular weight) and the content of related substances. Related substances are monosaccharides, proteins, organic acids, salts, and others.

The object of study were high-concentrated pectin extracts of beet pulp, apple and carrot pomace. Pectin extracts were obtained by hydrolysis of protopectin of prepared raw material by citric acid. Hydrolysis was conducted under vacuum during 2 hours at temperature of 60...80°C, pH of hydrolysis masses 2.5. This technological regime provides the process of extracting pectin substances with high qualitative values.

After extracting pectin substances by hot water and refining them from the insoluble impurities the extract contained 3...5% of solids and...2 0.58% of pectin substances.

To obtain pectin extracts in the dry form it is necessary to concentrate them to the most possible content of solids and pectin. At the concentration of pectin extract more than 18% DS and 10% PS it becomes inappropriate for the production, as a result of an increase in its viscosity. Besides, during concentration in a vacuum evaporator colored substances are formed as affected by temperature and air as a result of reaction melanoidin-formation and oxidation of phenolic compounds. In production rotary-film evaporator or membrane filters are used for the concentration of solutions. In this case pectin-containing solutions or extracts are less effected by temperature and duration of their concentration decreases .

Laboratory rotary vacuum was used for the concentration of pectin extracts. Concentration was conducted during 4...6 hrs at temperature of 60...70°C. During this time all the primary properties of pectin substances are retained.

During concentration of pectin extracts samples with different concentration of solids and pectin substances were selected. At temperature of 20°C the density and dynamic viscosity of the extracts were determined.

Investigation of dynamic viscosity was conducted using viscometer of Hepler [25].

The study of the density and dynamic viscosity of pectin extracts depending on the mass fraction of pectin at 20°C are shown in table. 4.11.

Table 4.11 – Density and dynamic viscosity of pectin extracts depending on the mass fraction of pectin

Parameter	Temperature, t °C					
	20	**30**	**40**	**50**	**60**	**70**
1	2	3	4	5	6	7
Beetroot pectin extract						
DS, %	18	15	12	9	6	3
PS,%	9.9	8.66	7.43	5.57	3.71	1.86
p, kg/m^3	1072	1062.5	1052.9	1038.6	1024.3	1010
$\mu \cdot 10^3$, Pa·s	3447.77	962.32	548.40	162.90	50.31	12.69
Apple pectin extract						
DS, %	18	15	12	9	6	3
PS,%	7.2	6	4.8	3.6	2.4	1.2
p, kg/m^3	1077	1063.6	1050.2	1036.8	1023.4	1010
$\mu \cdot 10^3$, Pa·s	671.46	367.66	171.45	44.15	27.21	8.3
Carrot pectin extract						
DS, %	18	15	12	9	6	3
PS,%	3.50	2.92	2.33	1.75	1.17	0.58
p, kg/m^3	1079	1065.2	1051.4	1037.6	1023,8	1010
$\mu \cdot 10^3$, Pa·s	27.93	19.86	11.86	7.27	4.34	2.24

We investigated these parameters depending on the temperature. The temperature range was selected from 20°C to 80°C, with measurement interval of 10°C, the results of the study are shown in table. 4.12.

Table 4.12 – Density and dynamic viscosity of pectin extracts depending on the temperature

Parameter	Temperature, t °C						
	20	**30**	**40**	**50**	**60**	**70**	**80**
Beetroot pectin extract CP=18 %, ПР=9.9 %							
p, kg/m^3	1072	1069	1067	1063	1060	1055	1047
$\mu \cdot 10^3$, Pa·s	3447.78	2252.63	1344.82	907.49	649.60	446.43	313.64
Apple pectin extract CP=18 %, ПР=7.2 %							
p, kg/m^3	1077	1071	1067	1063	1059	1054	1050
$\mu \cdot 10^3$, Pa·s	671.46	437.60	336.11	234.70	164.83	123.31	86.53
Carrot pectin extract CP=18 %, ПР=3.5 %.							
p, kg/m^3	1079	1076	1072	1066	1060	1055	1050
$\mu \cdot 10^3$, Pa·s	27.93	21.40	15.47	12.03	9.06	7.08	5.58

Apart from the results of density and dynamic viscosity of pectin extracts it is necessary to know the values of the surface tension of these solutions to calculate spraying and drying parameters. Depending on the value of the surface tension it is possible to define the initial droplet diameter when spraying etc. [42, 54, 63, 64]. The value of the surface tension of pectin extracts at maximum concentration of solids and pectin substances depending on the temperature is presented in table 4.13.

The surface tension of the liquid depends on the substances in solution. Some of them that are related to the surface-active substances (surfactants) can reduce surface tension. One of these surfactants is pectin which shows emulsifying and foaming properties [5].

Analysis of the obtained experimental values of the characteristics of pectin extracts helps to establish consistent patterns of change of parameters of density and dynamic viscosity depending on the concentration of solids and pectin substances and the change of density, dynamic viscosity and surface tension depending on the temperature at a constant concentration of solids and pectin substances [60].

Table 4.13 – The surface tension of pectin extracts

Parameters	Temperature, t °C						
	20	30	40	50	60	70	80
Beetroot pectin extract CP=18 %, ПР=9.9 %							
$\sigma \cdot 10^3$, N/m	57.866	57.292	57.102	57.061	56.523	56.477	51.017
Apple pectin extract CP=18 %, ПР=7.2 %							
$\sigma \cdot 10^3$, N/m	85.582	69.440	64.999	61.989	59.734	57.204	56.344
p, kg/m^3	1072	1069	1067	1063	1060	1055	1047
$\mu \cdot 10^3$, Pa·s	3447.78	2252.63	1344.82	907.49	649.60	446.43	313.64
Carrot pectin extract CP=18 %, ПР=3.5 %.							
p, kg/m^3	1079	1076	1072	1066	1060	1055	1050
$\mu \cdot 10^3$, Pa·s	27.93	21.40	15.47	12.03	9.06	7.08	5.58

2.1.7 Gelling ability of pectin extracts

Ability to gelling pectins that are obtained by changing various parameters of the processes of technology is one of the criteria for evaluating the effectiveness of technological processes of manufacturing pectin and pectin products. The study was conducted

with pectin extracts that were obtained from apple, carrot pomace and beet pulp using citric acid as a hydrolytic factor.

In technology of jelly products with pectin acids (citric, lactic) provide buffer capacity of the system of pectin-sugar-acid and inhibits dissociation of polygalacturonic acid which is one of the factors pectin gel formation [57]. That is, the presence of citrate ions in pectin extracts excludes the additional introduction of food acids. Key indicators of pectin that determine the type of gelation and its ability to form gels are molecular weight and degree of esterification. Highly-etherificated pectins (E = 68...78%) form gels in the presence of 60 ... 65% sugar and 1% acid, low-etherificated pectins (E = 35 ... 50%) can form gels at much lower concentration of sugar or even without it the presence of ions of polyvalent metals [2]. Therefore, we investigated samples of pectin extracts, pectin of which has the following characteristics:

- liquid apple extract, pectin content of 4% , the degree of esterification of 72%, molecular weight - 250000;
- dry apple extract, pectin content of 40%, the degree of esterification of 45%, molecular weight - 180000;
- liquid carrot extract, pectin content of 4%, the degree of esterification of 48%, molecular weight - 23000;
- liquid beetroot extract, pectin content of 4%, the degree of esterification of 42%, molecular weight - 22000.

Ability to gelling liquid apple pectin extract was determined in the system of pectin-sugar-acid, dried apple, carrot and beetroot – in the system of pectin-Ca ion-sugar (fig. 4.13). Calcium chloride was used a source of calcium ions calculating 40 mg of salt per 1 g of pectin.

Apple extracts 48...56 kPa have the highest gelation ability that allows using them as gelling agents in production of confectionery products of jelly group, beetroot and carrot ones have lower ability. Such extracts can be used as thickeners, stabilizers in the production of canned products, dairy products etc.

Gelationn ability varies for each type of pectin in a certain range of pH values. Therefore, the studies on the influence of pH environment on the ability of pectin extracts to gelation (fig. 4.14).

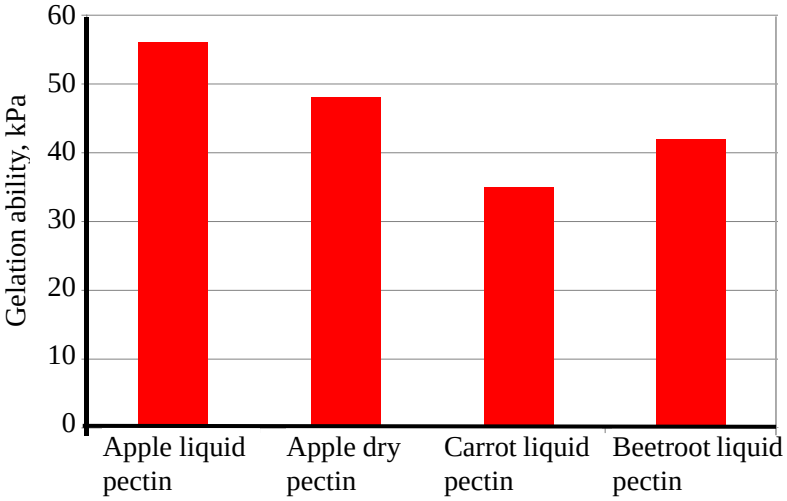

Figure 4.13 – Pectin extracts ability to gelation

The results of the investigation show that liquid apple pectin extract in the range of values of pH = 2.8 ... 3.6 has the maximum ability for gelation. The range of maximum gelation for low-etherificated extracts (apple, carrot, beet) is much wider and the reaction of environment is pH = 2.5 ... 4,8.

During the study of the ability to gelation of dried beet and carrot pectin extracts it was found that revealed that they do not form firm gel structures. It is explained by the fact that during the process of drying pectin substances undergo some changes, namely the degree of esterification (E = 28 ... 30) and molecular weight (10000 ... 16000) reduce. Such pectin extracts can be used as stabilizers in food environments or as biologically active additives in foods of therapeutic – prophylactic prescription.

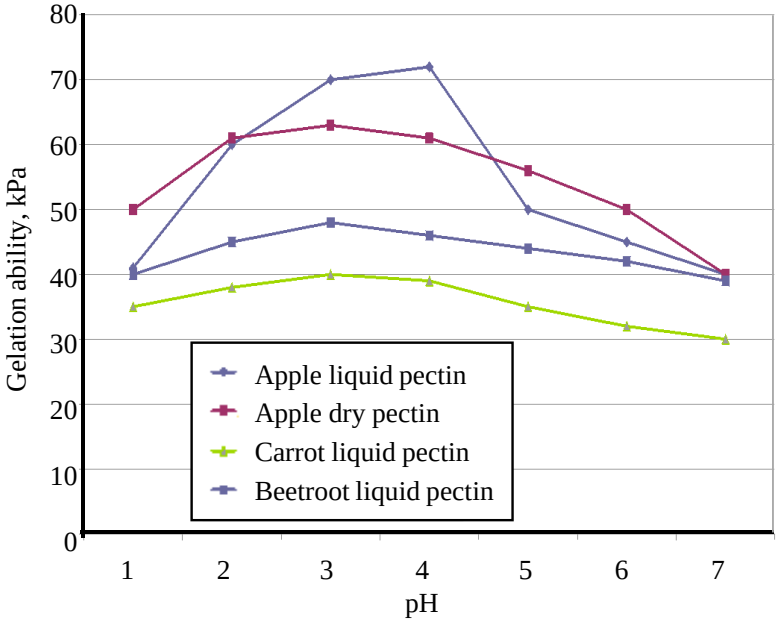

Figure 4.14 – Dependence of pectin extracts ability to gelation on the reaction of the environment

2.1.8 The process flowsheet of dry pectin extracts production.

The process flowsheet was developed based on the results of laboratory tests and analytical calculations and equipment for obtaining dry pectin extracts was selected [45-48, 50]. A distinctive feature is its non-waste technology, versatility, safety and environmental friendliness. Selection of equipment, piping and implementation of technological regimes were conducted according to the physical-chemical characteristics of pectin substances (active interaction with ions of metals, nonresistant to high temperatures, adsorption properties, viscosity) as well as the change in pH environment from 1.5 to 3 , 5.

Due to the fact that the equipment for pectin production is not specially made by machine-building enterprises, so the process flowsheet of production is composed with equipment of chemical and food industry (sugar, canning, dairy).

The process flowsheet of production of liquid and dry pectin extracts and pectin-containing food products with higher content of

pectin is presented in fig. 4.15.

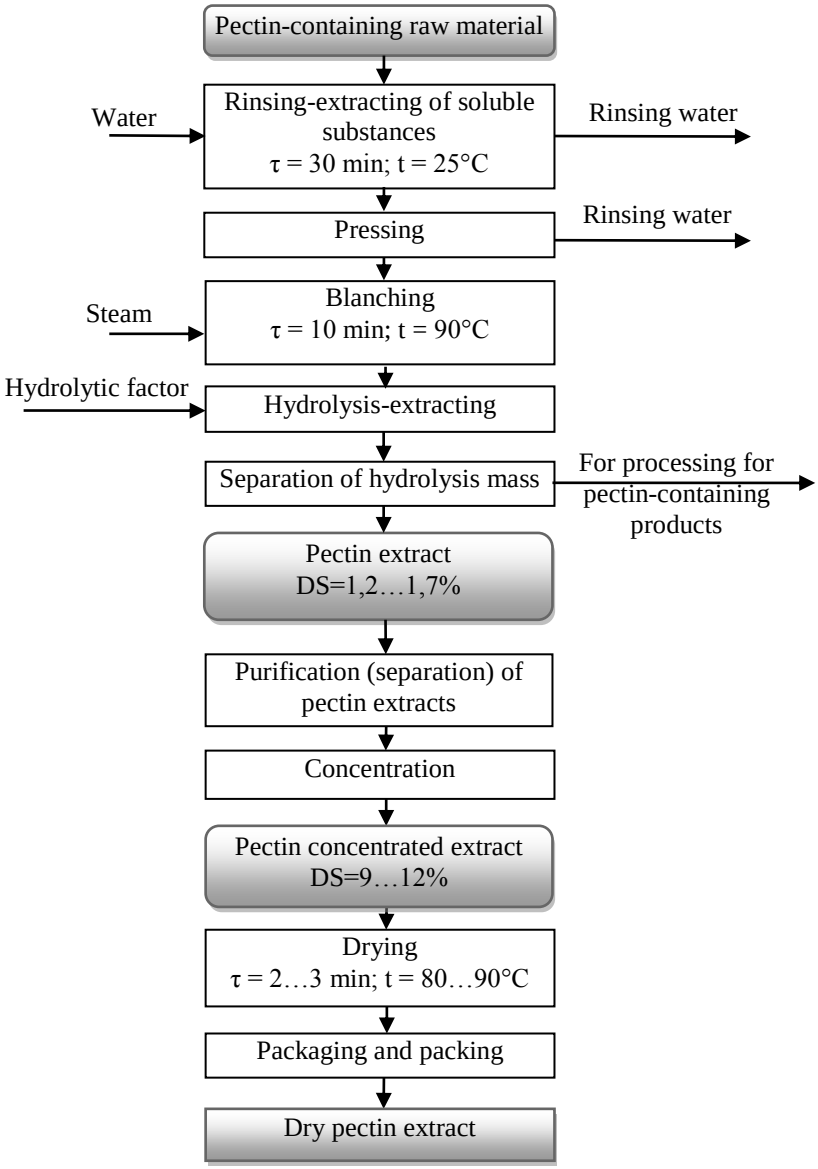

Figure 4.15 – The process flowsheet of dry pectin extracts production

Pre-prepared pectin-containing raw material enters the extractor, where it is mixed with drinking water in proportion of 1:3 with a temperature of 40...50°C and stays there during 15...20 min. For a better extraction of solvent ballast substances in relation to pectin raw material is separated from the free water on the separation sieve then it is pressed to humidity of 88...90%, then it is blanched at temperature of 90...95°C during 5...7 min. and delivered to the hydrolysis-extraction. Hydrolysis-extraction takes place in apparatuses of cyclic activity under vacuum 0,075 MPa for 120 min. Hydrolytic factor is prepared in a separate apparatus and it is delivered prepared to the hydrolyzer. After hydrolysis of protopectin, hydrolytic mass is pumped into the drain where separation of free extract from the hydrolysis mixture takes place. Separated extract is refined by separation and concentrated and dried in spray drying unit, after that it is packaged and packed in plastic bags of 25 kg.

If necessary pectin extract is neutralized to pH = 3...3,5 that in turn moderates concentration and drying conditions [58].

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3 TECHNOLOGIES BASED ON THE STUDIED STRUCTURE-FORMING AGENTS

3.1 Technology of jelly dishes

The initial stage of jelly dishes production is the washing and soaking of xerogels. According to the data obtained (section 1), the moisture absorption (We) of the structure-forming agents is conducted in the presence of modifiers. In the preparation of products based on gelatin in the presence of salts and alcohols We increases and the structure with additives reaches the required degree of moisture absorption after (40… 60) × 60 s, which allows to reduce the duration of the stage by (20… 30) × 60 s compared to the traditional technology. When sulfited polysaccharides are used, the presence of additives reduces moisture absorption, and We can be intensified by increasing the temperature.

Structure forming agent that the swelling with the modifiers dissolves in a water bath at a temperature of 75… 85 ° C after which the recipe components are added.

It is important to study the influence of prescription components on the action of modifying additives. Changes in the strength of the jelly depending on the concentration of gelatin in the prescription mixture (sugars 20%, citric acid 0.8%) were studied (Fig. 3.1).

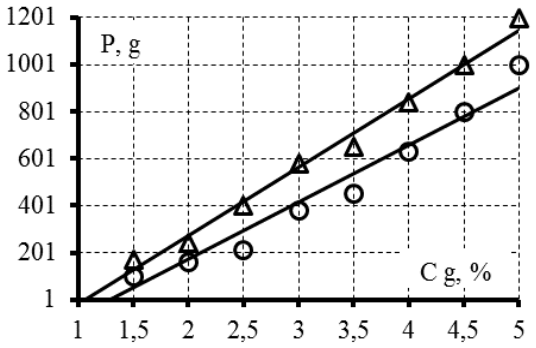


Figure 3.1 - Dependence of the jelly strength on the concentration of gelatin in the prescription mixture: 1 - gelatin, 20% sugar, 0.8% citric acid; 2 - gelatin, 0.8% SL, 0.3% SC, 0.25 Gk, 20% sugar, 0.8% citric acid

The graph shows that the gelatin concentrations studied (1 ... 5%), organic acids salts and polyatomic alcohols which were added, they helped to strengthen the jelly.

When modifiers are added to sulfited polysaccharides, the strength of the samples increases. Thus, the jelly strength of 2.4% agaroid is about P = 300 g. To achieve this value it is possible to reduce the concentration of the agaroid to 1.5%, furzeloran to 1.2% in the presence of 0.4% sodium lactate and 0.4 % glycerol.

From this it follows that in the prescription mixture containing additives-modifiers, it is possible to reduce the concentration of the jelly-forming agents. In this case, products obtained by organoleptic characteristics are not inferior to the control samples. Thus, in the preparation of jelly dishes with the traditional amount of the jelly-forming agent (3%), the jelly strength of the finished jelly is in the range of 380… 390 g. With the introduction of OAS and PAA in concentrations recommended the same strength of the finished dishe is achieved at a gelatin concentration of 2.2 … 2.3%, which is 20… 30% lower than the bookmark jelly-forming agent of the formulation according to the traditional recipe, and 30… 40% based on the agaroid.

The results of the influence of OAS and PAA on the jelly strength of agaroid in the presence of sugar are shown in table 3.1.

Table 3.1 - Influence of OAS and PAA on the strength of 4% jelly of agaroid in the presence of sugar

№	Concentration of additives, %				The strength of the jelly, g, in the presence of sugar		
	SL	SA	SC	Gl	0 %	10 %	20 %
1	0.4	-	-	-	550	690	927
2	-	-	-	0.4	390	590	793
3	0.4	-	-	0.4	740	1020	1325
4	-	0.45	-	-	635	715	960
5	-	0.45	-	0.4	720	995	1310
6	-	-	1.0	-	605	745	997
7	-	-	1.0	0.4	702	1065	1405
8	-	-	-	-	400	670	900

The analysis of the table data shows that the strength of the jelly with the addition of OAS and PAA in the presence of sugar is also increasing.

However, this amount of sugar (up to 20%) reduces the strengthening effect of the additives.

The results obtained indicate the possibility of using jelly-forming agents with qualitatively modified properties in the production of jelly dishes with different concentrations of sugar in the jelly mass.

The study of functional and structural-mechanical properties of jelly-forming agents of different nature with modifiers allowed to develop recipes and technologies of jelly culinary products using salts and alcohols. These schemes include a number of general technological steps: moisture absorption of the jelly-forming agent, its dissolution and jelly-forming. Depending on the technology and recipe, there may be other stages of the process, such as whipping jelly. Jelly dishes and products are prepared on gelatin, agar, furcellaran and agaroid according to their interchangeability, taking into account their jelly-forming ability.

When cooking with the use of a jelly-forming agent, various ingredients are included in the recipe, which exert a certain influence on the structure formation of the dish - egg protein, sour cream, cream. In these formulations, gelatin acts as a jelly-forming agent.

Developed recipes are presented in table. 3.2… 3.4, technologies of jelly products with the use of modifying additives in fig. 3.1… 3.3.

Table 3.2 - Recipe "Jelly Fruit or Berry"

Name of raw materials	Gross weight, g	Net weight, g
Fruit or berry syrup	250	250
Water	780	780
Gelatin	22	22
Sodium lactate	8	8
Sodium citrate	3	3
Glycerol	2	2
Citric acid	1	1
Finished product output	-	1000

Table 3.3 - Recipe "Lemon mousse"

Name of raw materials	Gross weight, g	Net weight, g
Lemons	190	80^{x}
White sugar	250	250
Water	770	770
Gelatin	20	20
Sodium lactate	8	8
Sodium citrate	3	3
Glycerol	2	2
Finished product output	-	1000

^{x} – mass of juice

Table 3.4 - Recipe "Apple sambuc"

Name of raw materials	**Gross weight, g**	**Net weight, g**
Apples	795	700
White sugar	200	200
Eggs (proteins)	2 pieces	48
Water	420	420
Gelatin	11.3	11.3
Sodium lactate	2.0	2.0
Sodium citrate	0.8	0.8
Glycerol	0.7	0.7
Finished product output	-	1000

The above technological schemes are different from the traditional by using of modifying additives and reduced amount of jelly-forming agent. Adding the proposed ingredients is carried out at the stage of swelling of gelatin. This reduces the swelling duration of the jelly forming by (20… 30) × 60 s.

Thus, the technology of jelly dishes based on jelly-forming agents of different nature with modifying additives is developed, scientifically substantiated and practically implemented. The technological researches made it possible to develop recipes and technologies of dishes and culinary products (jellies, mousses, sambuc, creams, cakes) basis on the jelly-forming agents with qualitatively changed functional properties. These recipes and technologies are included in the collection of recipes for sweet

dishes, confectionery and bakery products using modified jelly-forming agents.

The range of dishes and products based on gelatin, agaroid, furcellaran and agar can be significantly expanded. This is facilitated by the preparation of the introduced modifiers, which will reduce the cost of scarce, expensive polysaccharides by 30… 40% and gelatin by 25… 28%.

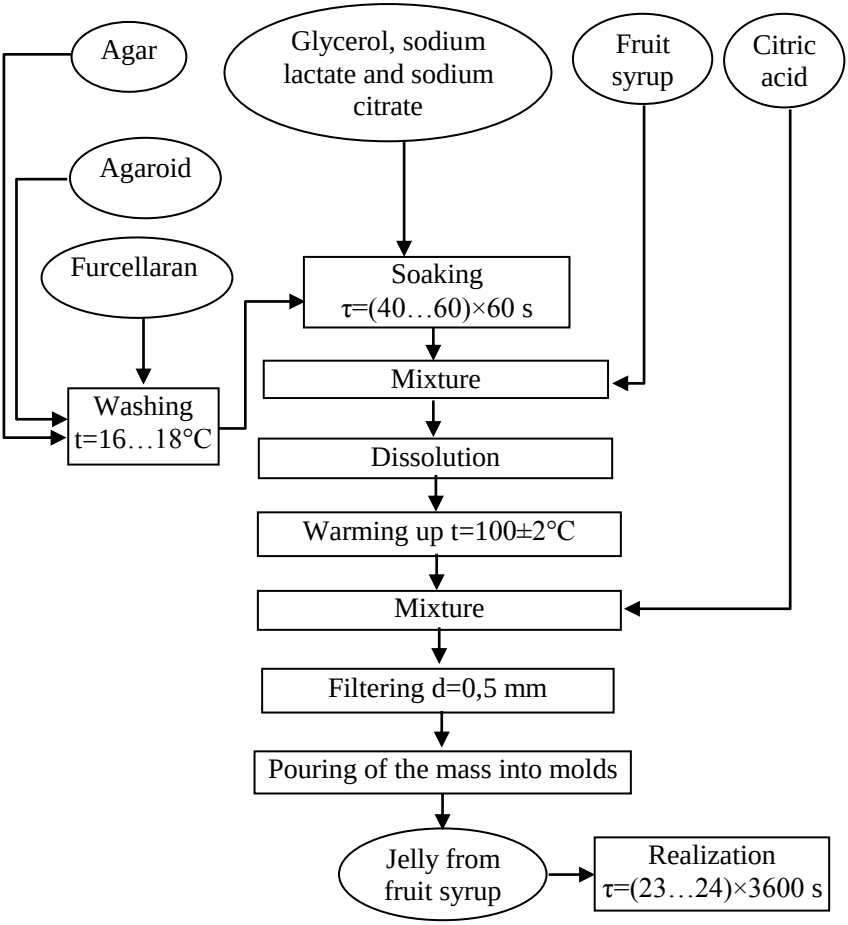


Figure 3.2 - Technological scheme of jelly made of fruit or berry syrup based on red seaweed with modifying additives

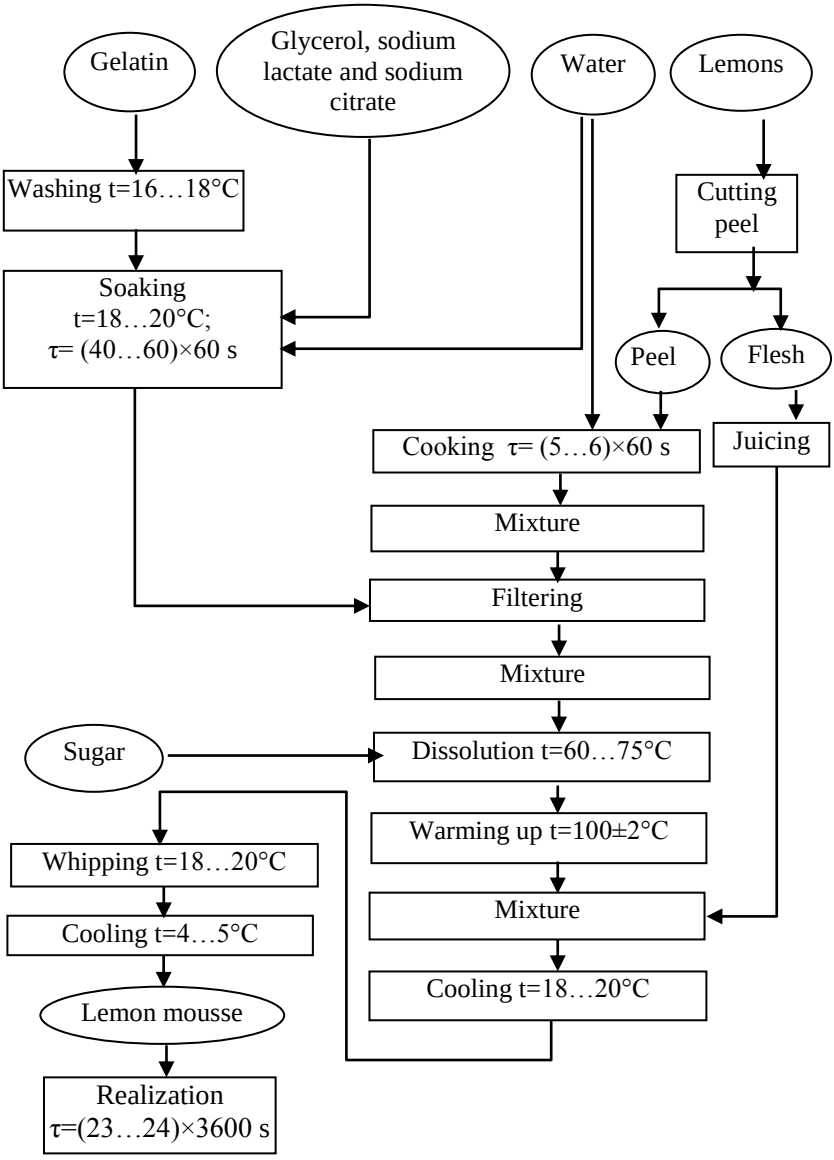


Figure 3.3 - Technological scheme of lemon mousse based on gelatin with modifying additives

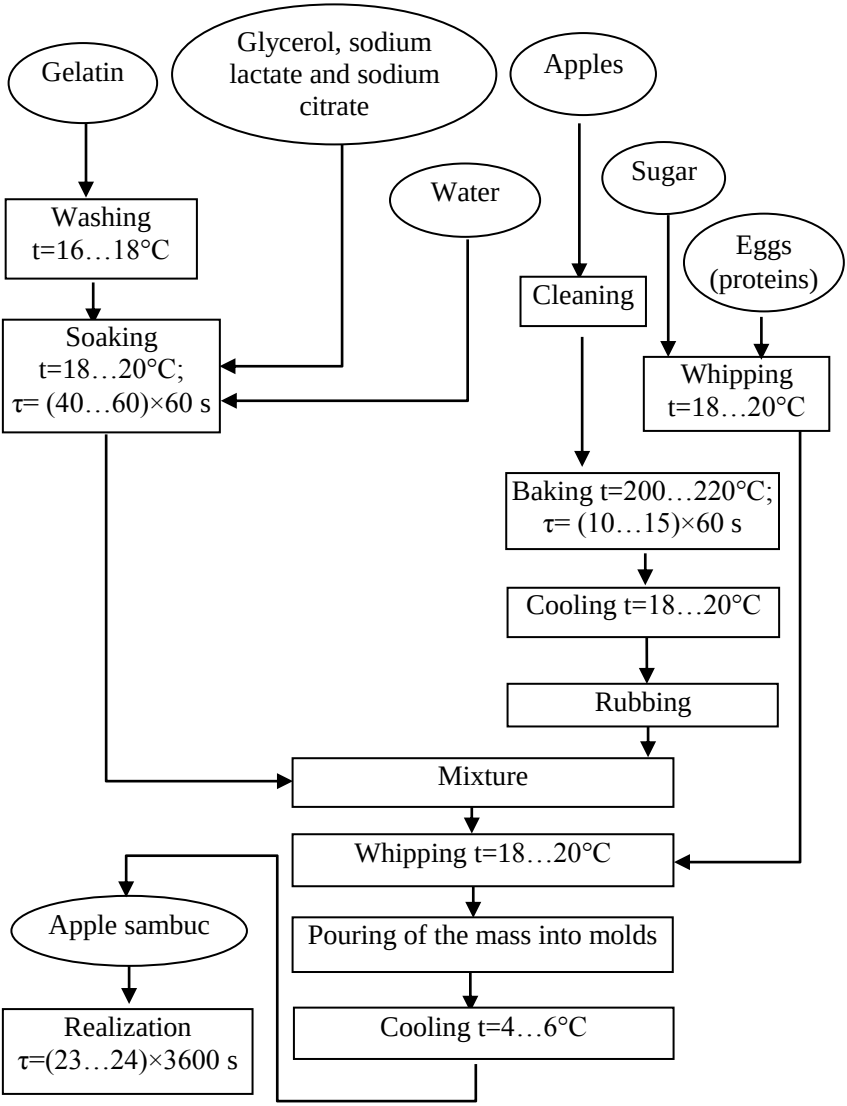


Figure 3.4 - Technological scheme of apple sambuc based on gelatin with modifying additives

3.2 Technology of culinary products using milk protein

The study of physicochemical and structural-mechanical properties of gelatin and its mixtures with food components suggests a wide range of its use in obtaining products of a gelatinous structure. The range of products can be wide, since gelatin is easily mixed with food ingredients, in particular, with milk protein.

The ability of polyatomic alcohols together with organic acids salts to reduce the consumption of gelatin by an average of 25… 28% is the basis for the technology of sweet and salty curds using milk protein.

Analysis of the properties of the system gelatin:milk protein shows that sweet and salty curds can be obtained from it.

Milk protein, which was obtained by the method of thermoacid coagulation, meets these requirements to the greatest extent. The study of the influence of technological factors on the process of structure formation of the system confirmed the possibility of obtaining sweet and salty cottage curds. It was found that in order to provide the required organoleptic characteristics of the products obtained, the protein should be characterized by a viscosity $(2{,}16…5{,}10)\times10^{6}$ Pa×s and a shear deformation $(7{,}28…16{,}12)\times10^{-2}$.

Known methods of thermodynamic coagulation do not allow to obtain a protein with marked structural and mechanical properties. In this regard, the milk protein technology was developed, which is based on changes in the temperature regimes of coagulation. It involves heating the milk to 91… 95 ° C, cooling to 65… 80 ° C, mixing with serum, which is 30% by volume of the coagulation mixture, with an acidity of 85… 95 ° T and temperature of 18… 20 ° C.

Protein obtained by the proposed method has a viscosity $(2{,}16…5{,}10)\times10^{6}$ Pa×s and shear deformation $(7{,}28…16{,}12)\times10^{-2}$.

Obtaining a gelatinous structure of curds with given organoleptic properties depends on many factors and, first of all, on the mixing process. A stable process of jelly formation is ensured by

mixing to a uniform consistency of gelatin solution with prescription components at 55… 65 ° C for 30×60 s.

However, it is unacceptable to reduce the concentration of structure-forming agent below 1.6% by weight of products. Apple powder, salt and protein increase the strength structure, and sugar - reduces.

The complex of researches made it possible to scientifically substantiate the technology of preparation and recipes of sweet and salty curds (Table 3.5, Fig. 3.5… 3.6).

Depending on the place where the curds is cooked, different approaches can be implemented to ensure the technological process.The developed product is characterized by high biological value (Table 3.6).

Table 3.5 - Recipe of sweet and salty curds

Name of raw materials	Net weight, kg per 1 ton of finished product	
	salty curd	sweet curd
Milk 3.2% fat	6000.0	5000.0
or skimmed milk	7200.0	6000.0
Milk serum	2638.0	2212.0
Milk protein	864.0	720.0
White sugar	-	102.0
Citric acid	-	7.2
Apple powder	-	51.0
Gelatin	18.0	16.7
End of Table 3.5		
Sodium citrate[x]	10.0	10,0
Glycerol	4.0	4,0
Table salt	19.0	-
Vanillin	-	-
Total	1023.0	1023.0
Finished product output	1000.0	1000.0
Losses of mixing, forming, packing, transportation, kg	23.0	23.0

[x] – Sodium citrate is used as a 58% solution

Table 3.6 - Chemical composition of curds

Indicators	Contents, %	
	sweet curd	salty curd
Moisture	58.9±1.1	58.8±1.1
Proteins (OA.6.25)	13.5±0.8	13.9±0.6
Lipids	11.6±0.7	11.0±0.7
Carbohydrates	14.8±0.4	15.0±0.6

Curds are generally characterized (in % to total protein) by high levels of casein (75… 85%) and serum proteins (11.6% 4 14.0%).What cannot be said about products from cottage cheese in which serum proteins are not present.

Thus, the shelf life and sale of cottage cheese and the products made from them should not exceed 24 hours from the moment of their preparation at a temperature of 2… 6 ° C.

Curds can be made from whole and skim milk at the dairy industry in the form of curds salty, sweet and sweet in the glaze and used in restaurants to make them sandwiches, cold dishes, snacks and dessert dishes.

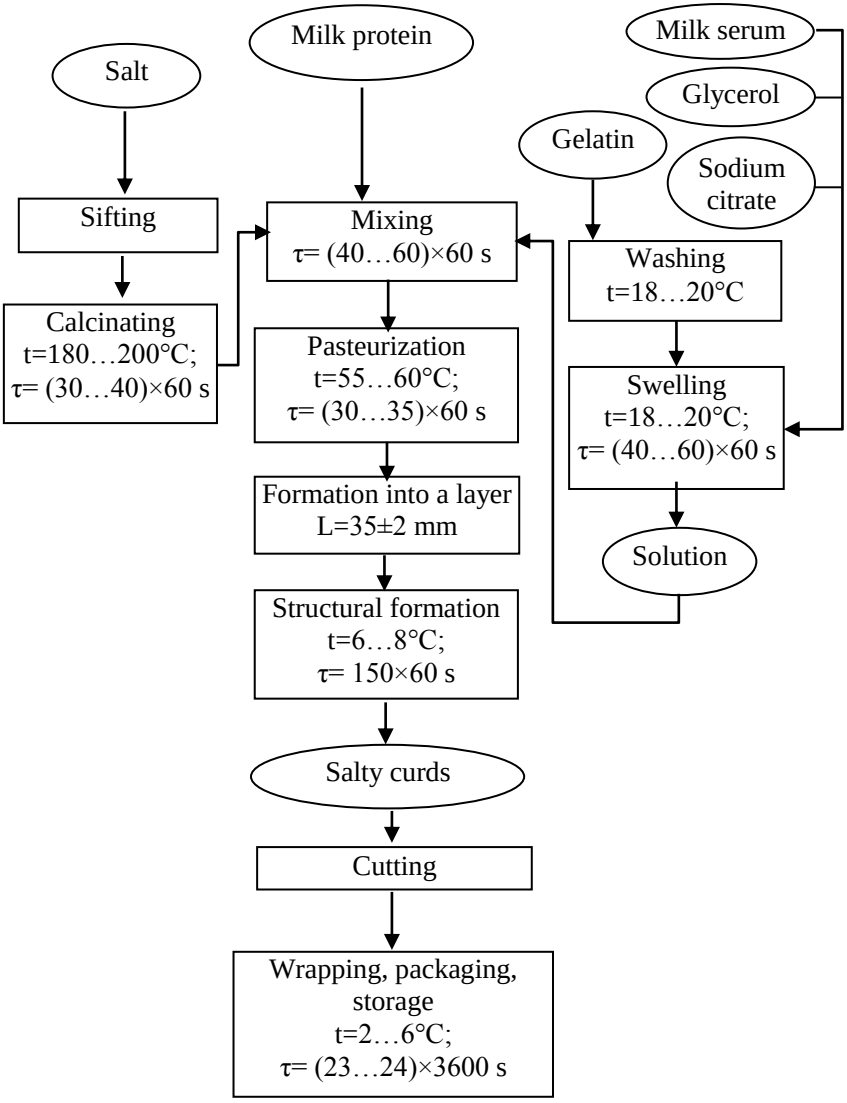


Figure 3.5 - Technological scheme of salty curds

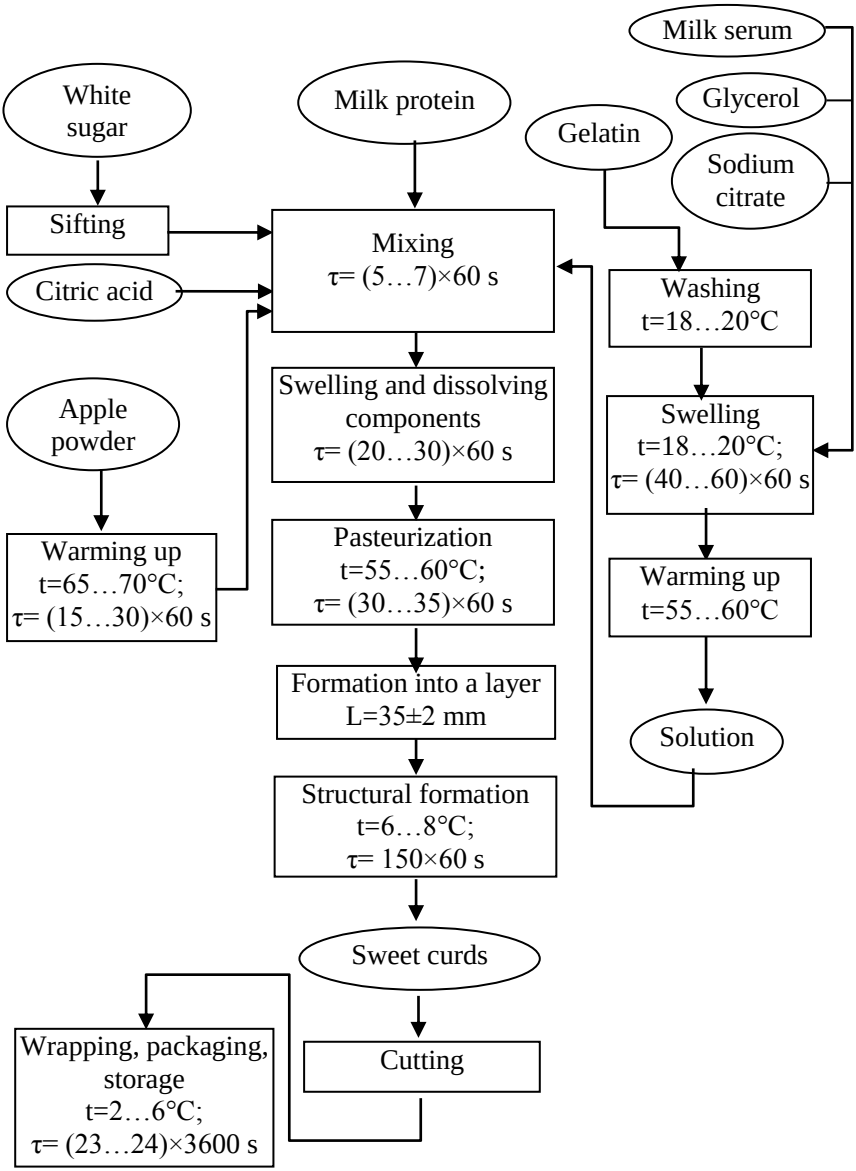


Figure 3.6 - Technological scheme of sweet curds

3.3 Confectionery technology

3.3.1 Production technology of jelly marmalade

The developed method of qualitative changes in the functional properties of the jelly forming agent of sulfited polysaccharides using organic and inorganic acids and polyatomic alcohols can be used to obtain various jelly products, including to obtain marmalade, taking into account the specifics of the technology.

When developing new technologies, it is necessary to take into account the parameters and characteristics of existing technologies and equipment.

The production of marmalade in confectionery factories is higher than the production of jelly products at food establishments.

An important factor to consider when creating a new technology is an organoleptic evaluation that meets the tastes of consumers and the requirements of normative documents (DSTU) for this type of products. A certain ratio of sugar, treacle, acids, jelly forming agent, aromatic and other substances can affect the formation of the jelly, as well as the quality indicators of marmalade - appearance, taste, smell. It is therefore necessary to maintain the approximate constancy of this ratio.

According to the requirements of DSTU jelly marmalade has a moisture content of 15… 23%. In prepared formulations, the humidity value is 18 ± 1%.

Considering this, it is possible to conduct the process of boiling the recipe mixture with a reduced amount of the jelly forming agent to the solids content, which is similar to the traditional technology.

When studying the technological characteristics of jellies of agaroid , which change under the action of modified additives, it was noted that in the presence of OAS and PAA, the dynamic viscosity of agaroid solutions increases compared to samples without alcohol. Increasing the viscosity of the recipe mixture may prevent the pouring of the mass through the holes in the pour funnel. Therefore, it is necessary to investigate changes in the viscosity of agaroid solutions of different concentrations with and without glycerol (Table 3.7).

Thus, it can be argued that the process of pouring jelly mass in the presence of modifying additives and a reduced number of jelly

forming agents can be carried out on the existing technological lines.

Table 3.6 - Changes in the dynamic viscosity of agaroid-based systems with the addition of modifying additives

№	Composition of the system			Viscosity $\eta \times 10^{-2}$ Pa×s
	Agaroid, %	Lactate Na, %	Glycerol, %	
1	2.5	0.4	-	31.1±0.4
2	2.0	0.4	-	30.3±0.4
3	1.5	0.4	-	29.2±0.3
4	1.0	0.4	-	28.3±0.3
5	2.5	0.4	0.4	32.3±0.3
6	2.0	0.4	0.4	31.5±0,3
7	1.5	0.4	0.4	30.2±0.3
8	1.0	0.4	0.4	29.4±0.3

Unlike the traditional method, according to the technologies offered glycerin, sodium chloride and sodium lactate are introduced at the stage of soaking lasting 60×60 s in the last 20×60 s swelling of the polysaccharide at a water temperature of 16… 18 ° C, such conditions provide a sufficient speed of the swelling process, which goes most intensively in the first (30… 40)×60 s swelling.

It is necessary to boil a jelly-forming agent with sugar syrup to a solids content of 72 ± 1%, depending on the modification method. Such recommendations allow to obtain products with appropriate structural and mechanical parameters and to meet the requirements of DSTU.

The data characterizing the chemical properties of jelly marmalade indicate that modifying additives introduced slightly alter the reducing substances, active and titratable acidity. Due to the increase of the solids content in the jelly mass, the amount of reducing substances and titratable acidity increase insignificantly, and the active one decreases.

In the process of storage of marmalade, which was obtained on the basis of the jelly-forming agent with modifying additives, the quality indicators change markedly. Moreover, the quality of the product is significantly influenced by temperature and storage time. With increasing temperature and duration of storage, the structure of marmalade strengthens, the active acidity while decreasing.

The technological scheme of production of jelly molded

marmalade based on sulfited polysaccharides with modifying additives is presented in Fig. 3.7.

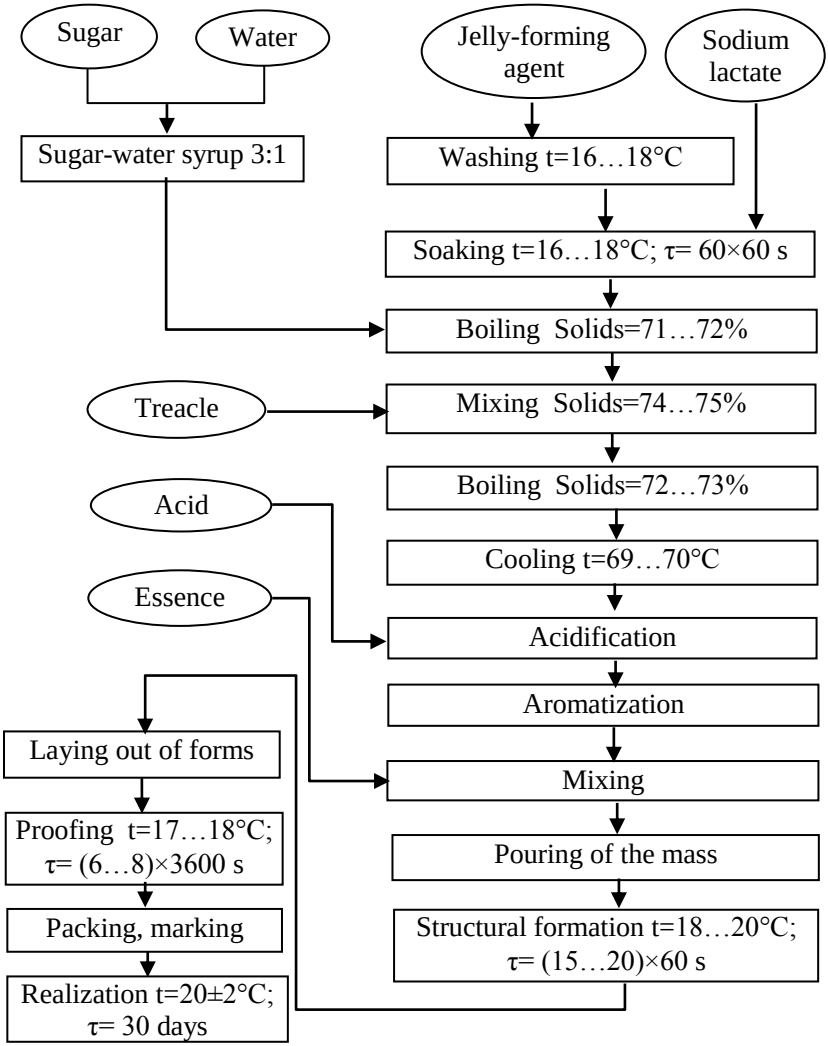


Figure 3.7 - Technological scheme of production of jelly molded marmalade, based on jelly-forming agent of red seaweed by pouring into sugar with the addition of ingredients that qualitatively alter the functional properties of jelly-forming agent

3.3.2 Production technology of jelly candy

The proposed method for improving the jelly forming ability of sulfited polysaccharides with the use of Na - CMC and $FeCl_3$ additives was used in the development of the technology of obtaining jelly candies.

The process of structure formation plays a large role in the production of candies, since the choice of a rational technological mode of production depends on the speed of jelly formation of the candy mass and the strength of the jelly.

When developing a new technology that allows to reduce the cost of the jelly forming agent, the main requirement was compliance with the requirements of the DSTU, which is controlled by indicators in the process of obtaining products.

Model systems have been studied the way of qualitative changes in the functional properties of agar, furcellaran and agaroid with the addition of modifying additives. However, the cases of candies includes a number of ingredients, which undoubtedly influnce on the structure formation process and mechanical strength of the gel. Thus, the composition of the recipe (semi-finished product of case) includes up to 69% sugar, 3.3% treacle, as well as in small quantities of sodium lactate, citric acid, different essences, ethyl alcohol, furcellaran .

The technological scheme of obtaining jelly candies consists of the following operations: at first jelly forming agent is subjected to washing under running water at temperatures not higher than 20 ° C for 30 × 60 s, soaking at the same temperature not more than 60 × 60 s. At the end of soaking, a 5% solution of sodium carboxymethyl cellulose is added. The prepared mixture is transferred to an open container in which the sugar syrup is prepared. The system boils to 65 ... 67% of solids and then treacle and sodium lactate are added, while the solids content is at the level of 72 ... 73%. After cooling to 70 ° C, 50% citric acid solution, essence, ethyl alcohol and chlorine iron solution are added to the mixture. Stirred and filtered jelly is pouring into stamped starch cells, where, for (15… 24) × 3600 s, the process of forming the jelly mass of candy canes is carried out.

Starch-free cases are glazed with chocolate glaze, cooled, wrapped, packaged.

In jelly candies, as in marmalade, the sugar contained in large quantities has a significant effect on the process of jelly formation [1]. In this regard, the effect of the dehydrating agent on the mechanical strength of the jelly was studied (Table 3.7).

The obtained data indicate the strengthening of the structure when introduced into the system of sodium carboxymethyl cellulose and iron chloride.

Thus, the strength of the 1.5% furcellaran jelly is 180 g, after the addition of Na-CMC and $FeCl_3$ the jellies are strengthened and reach 243 g. The increase in sugar in the system also helps to strengthen the structure. According to the data obtained, the modified additives are capable of 30… 35% increase in the strength of 1.5% furcellaran gel.

From the results obtained (Table 3.7), it follows that the joint introduction of sodium chloride and iron chlorine is not conducive to the strengthening of the structure and it is at the level of strength of the sample, which includes Na-CMC and $FeCl_3$.

Table 3.7 - Influence of sugar on the jelly strength of the candy cases in the presence of additives

The composition of the case, %			**Strength of 1.5% jelly of furcellaran, g at sugar content, %**				
Na-CMC	**$FeCl_3$**	**NaCl**	**0**	**15**	**30**	**45**	**60**
-	-	-	180	272	368	435	620
0.1	-	-	203	289	391	472	683
-	0.12	-	237	341	469	548	794
-	-	0.2	228	336	473	540	781
-	0.12	0.2	220	330	464	534	769
0.1	0.12	-	243	361	495	585	837
0.1	-	0.2	240	368	494	592	835
0.1	0.12	0.2	241	360	492	580	830

The introduction of three additives - Na-CMC and $FeCl_3$ and NaCl also does not change the magnitude of the jelly strength compared to the jelly, where there are Na-CMC and Fe $FeCl_3$. Thus P = 825…835 g.

From the obtained results it follows that in the production of jelly candies or other jelly products based on agaroid and furcellaran as modifying additives, you can use sodium carboxymethyl cellulose and sodium chloride, and when obtaining products on the basis of agar, furcellaran and agaroid - Na-CMC and $FeCl_3$

The action of each salt in combination with sodium carboxymethyl cellulose is equally effective, except for the agar. In this case, sodium chloride is added when soaking the jelly forming agent, and chlorine iron - in the finished mixture before pouring of mass into molds.

The joint introduction of Na-CMC and one salt increases the temperature of the jelly formation of the system to 51… 54 ° C. therefore, reducing the expenses of furcellaran will not adversely affect the structure formation process.

The strength of the control sample (Table 4.8) is 670 g, and the jelly, containing sodium carboxymethyl cellulose and chlorine iron - 625 g. Such a decrease in strength does not affect the quality of the jelly cases of candies.

Table 3.8 - Indicators of the amount of solids and strength of the control and test jellies of the candy cases

Composition of candies, %	Solids content,% at the end of the boil	Strength, g
1	2	3
white sugar 60.0	72.0±0.5	652
treacle 3.3		
Na-CMC 0.1		
$FeCl_3$ 0,12		
ethyl alcohol 2.0		
citric acid 0.6		
essence 0.05		
sodium lactate 0.4		
furcellaran 0.88		

Continuation of Table 3.8

1	2	3
white sugar 60.0	72.0±0.5	670
treacle 3.3		
ethyl alcohol 2.0		
ethyl alcohol 0.6		
essence 0.05		
sodium lactate 0.4		
furcellaran 1.19		

The technological scheme of obtaining jelly candies on the example of "Arcadia" candies is presented in Fig. 4.8.

The quality of jelly candies during storage is influenced by temperature and shelf life. From the data obtained, it follows that there is a correlation between the magnitude of the reducing substance and the strength of the jelly case. With the increase of reducing substances, the structure of products is strengthened. Keeping the product at a higher temperature promotes the jelly strength to a greater extent and the growth of reducing substances. The active acidity in this case is reduced.

Thus, the obtained results allow to conclude that the developed technologies and recipes of jelly candies based on sulfited polysaccharides with the addition of sodium carboxymethyl cellulose and chlorine iron allow to reduce the consumption of agar up to 22%, furcellaran - 35% and agaroid - 40%.

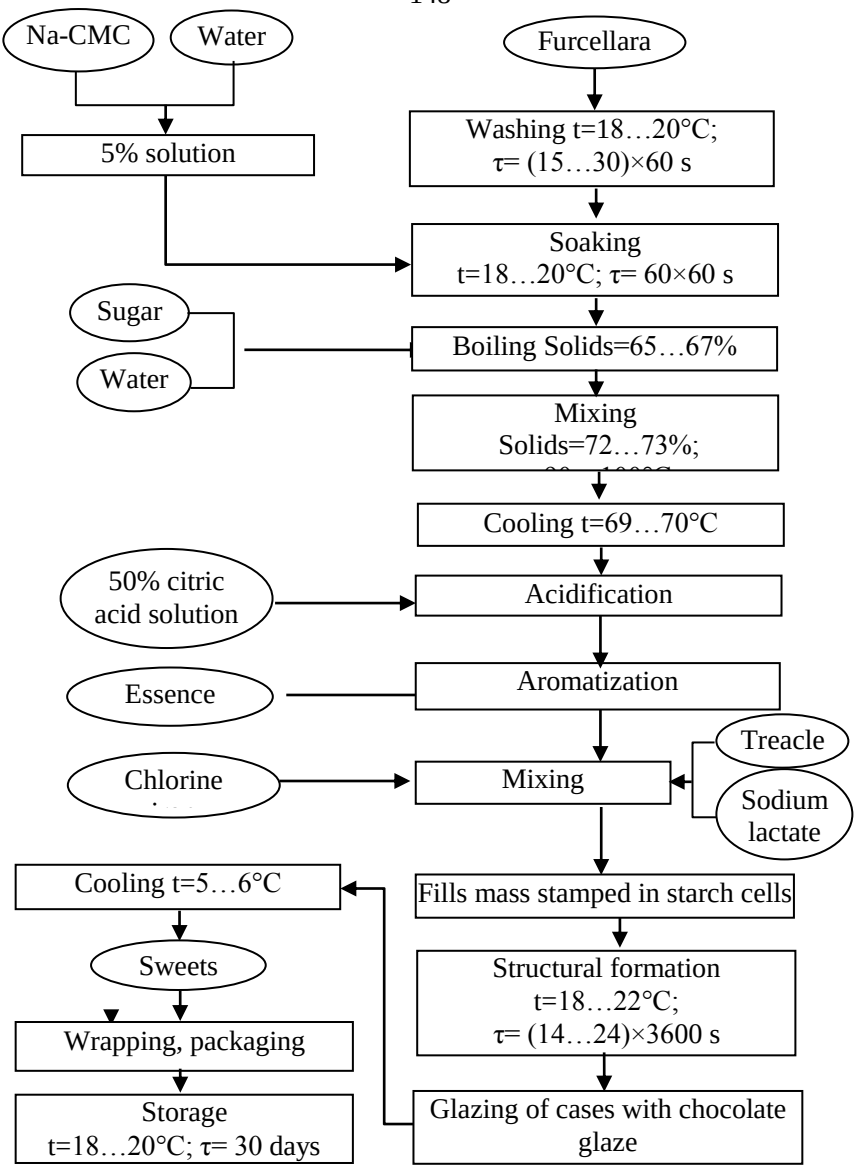


Figure 3.8 - The technological scheme of "Arcadia" jelly candies based on furcellaran with the addition of sodium carboxymethyl cellulose and chlorine iron

3.3.3 Technology of cakes

In a wide range of food products, sweet dishes and confectionery with foam structure are particularly popular with consumers. However, despite the high consumer demand, their actual production does not meet the needs. The supply and demand mismatch is explained by the complexity of the process and the lack of sufficient ingredients [2].

Traditional zefir are made by boiling sugar-agar-treacle syrup to solid content (84… 85%). Considering the fact that for the boiling of the syrup together with the treacle and structure-forming agent, steam and special steam boilers are needed. The technology of obtaining zefir based on fruit jam is proposed. Feature of the developed technology is whipping of egg protein with sugar, jam and agar-sugar syrup. The zefir mass obtained from the pastry bag is packed into wafer cups (Table 3.9). The recipe of zefir mass for the cake "Wafer cup with zephyr" is presented in table. 3.9.

Table 3.9 - The recipe composition of zefir for cake "Wafer cup with zefir "

Name of raw materials	Mass fraction of solids	Raw material consumption per 1000 pieces of finished product, g	
		in reality	in solids
Egg protein	12.0	6000.0	720.0
White sugar	99.85	3000.0	2995.5
Apple jam	66.0	22000.0	14520.0
Agar	85.0	210.0	178.5
Citric acid	98.0	100.0	98.0
Essence	-	6.0	-
Glycerol	100.0	0.6	0.6
Total raw materials		31316.0	18333.5
Finished product output		27.5	17.16
Losses of solids	7.3		

The solids content of the resulting mass is 62.7 ± 0.4%, the density is 565 ± 45 kg / m3, the active acidity is pH = 5.23 ± 0.03 and the pore radius is 24… 128 μm.

According to the technology developed, it is possible to get zefir mass, which will expand the range of whipped products at food businesses.

The technological scheme of obtaining the cake "Cup wafer with zefir" is presented in Fig. 3.9.

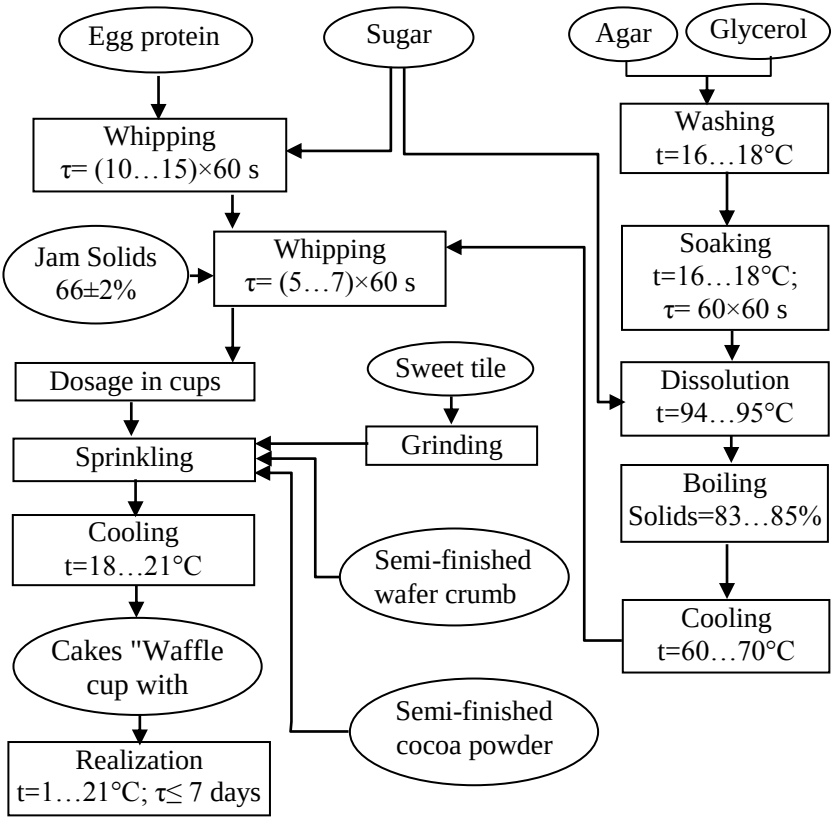


Figure 3.9 - The technological scheme of the cake "Wafer cup with zefir"

3.4 Encapsulated product shell technology

3.4.1 Agar-based shell technology

The technology of salmon caviar analog is based on the method of extrusion microencapsulation of coaxial tubes on the principle of "pipe in pipe". The jelly formation agent enters the outer tube, and the contents of the granules - on the inner. The content at the outlet of the pipe envelops thesolution of jelly formation agent due to their immiscibility with each other and enters a moist environment (corn or sunflower oil). The outlet opening of the outer pipe ends with a device which, due to the annular hydraulic impact, periodically divides the jet of the droplet components with a given frequency. The thickness of the granule shell is easily adjusted by changing the gap between the tubes. The formed granules are moved in a column with oil (forming medium) to the complete structuring of the shell and then separated.

It was found that the viscosity of the structure-forming agent used as heat-resistant and transparent shells supplied by an external pipe with a diameter of 4×10^{-3}m and a velocity of $1{,}0\times10^{-5}$m^3/s should be within $4{,}5\times10^{-2}\ldots1{,}0\times10^{-1}$Pa×s since the viscosity of the structure-forming agent used in the encapsulation is limited, it is necessary to take the choice of the jelly-forming agent and investigate its rheological characteristics. Given the functional properties of fikokoloids, agar provides the necessary organoleptic characteristics of the granules to the greatest extent possible. With this the concentration of phycoloids is at 4%. A similar change in the viscosity of the agar solution proved to be agile when receiving the capsules.

Those, the viscosity of 4% agar with modified additives (0.1% sodium lactate and 0.3% glycerol) at 90 ° C is slightly but above the control. Lowering the temperature increases the viscosity and increases the Δ S relative to the original sample. At temperatures below 50 ° C, the viscosity increases significantly, which is a positive factor in the formation of the jelly shell granules. Such a change in viscosity at the same temperature, compared to the control sample, increases the rate of jelly formation of shell, which reduces energy consumption for cooling the forming medium and reduces fikokoloids consumption. The rapid increase in viscosity and strength of the jelly formed by the cooling will significantly reduce the residence time of the granules in the cooled environment.

Optimal results of encapsulation were achieved at agar temperature of 70 ... 80 ° C, with a viscosity not exceeding 10×10^{-1}Pa×s. It is known that the formation of granules with a given thickness of the shell from the jelly solution, which is not mixed with it in a purely physical process, and is determined by the surface tension at the interface of the forming medium - a solution of the jelly-formation agent containing granules and their viscosity.

The data on the study of the relative arithmetic strength of the jelly shell of the granules, depending on the duration of their stay in the forming medium shows that due to the structuring that occurs in the aqueous solution of 4% agar at a temperature of 2 ... 18 ° C mechanical strength of the shells quickly increases from 0 to 30×10^{3} Pa×s, especially in the first seconds of being in a cooled environment. A significant deviation of the relative average strength is observed only in the initial period of shell structuring . After (5… 6)×60 s granules stay in the oil, the strength of the shell does not depend on temperature and reaches its maximum value due to the concentration.

The relative average mechanical strength of the granule shell after (5… 6) × 60 s stay in oil with a temperature of 2… 18 ° C is on average 96… 100% of the relative average mechanical strength of the granule shell of the same batch after their storage for 22 hours at temperatures of 4… 8 ° C.

The introduction of organic acid salts and polyatomic alcohol into the solution of the jelly formayion agent allows to save up to 30% of the agar to obtain the jelly shell in the production of protein red caviar.

3.4.2 Agaroid-based shell technology

Developed technology for producing shells of granule analogue salmon fish caviar requires significant agar expenses.

In this regard, it was advisable to explore the possibility of using an agaroid to obtain the jelly shell of granules.

As shown by previous experimental studies of the use of agaroid in the native state to obtain the shell is impractical, since the melting and solidification temperatures of its jelly is low, which violates the stability of the capsulation process. Increasing the concentration of agaroid in the solution does not allow it to be used in connection with the limiting value of viscosity. With this in mind, a new technology for obtaining an agaroid-based shell with

qualitatively modified functional properties is proposed. To this end, organic acid salts and polyhydric alcohols are added to the fikokoloid. When choosing the concentration of the agaroid in the solution, the allowable viscosity to work on the installation, jelly strength, melting and solidification temperatures, structuring rate and organoleptic characteristics of the finished product were taken into account.

Experimental data of the dependence of the jelly strength of the agaroid on the concentration of organic acids salts show that with significant amounts of additives, the maximum strengthening is observed at a content of 5… 7% of them in fikokoloid. In the presence of sodium acetate, jelly have the highest strength and reaches 2000 g. The experimental data made it possible to establish that the most rational is a system containing 5% agaroid, 5% sodium acetate and 0.3% glycerol.

Technological scheme of production of red protein caviar using agaroid for the preparation of the shell is presented in Fig. 3.10.

The study of the rate of structure formation showed that the relative arithmetic strength of the granules shell based on agaroid with the addition of significantly higher strength of the shell obtained on a pure agaroid. Moreover, the required value of the strength of the granules shell reaches already after (12… 14)×60 s stay in the forming medium with a temperature of 12 °C, and with a temperature of 2 °C - after (8… 10)×60 s, while the shell granules on pure agaroids do not reach 200 Pa × 10^2.

The formed granules are subject to washing with water from oil and cooking, swell and absorb the additive that gives the taste and smell of the product.

In order to exclude the process of diffusion from the jelly shell of salts and alcohol, an additional technological step of washing the granules from oil with a solution of table salt was proposed, which eliminates contact with water and thus stores the ingredients in the jelly.

The washed shell of the granules for 5×60 s with a 5% solution of sodium chloride has a melting temperuture of 63 ° C, and after 20 × 60 s - 89 ° C. In the case of increasing the salt concentration twice the melting temperuture is 83 ° C and 93 ° C. Washing with 10% sodium chloride solution indicates that the combination of two technological processes (washing of shell and

salting of granules) helps to reduce the technological scheme of producing caviar and significantly increase the melting temperuture of the shell. In the shell contains no more than 5% of sodium chloride.

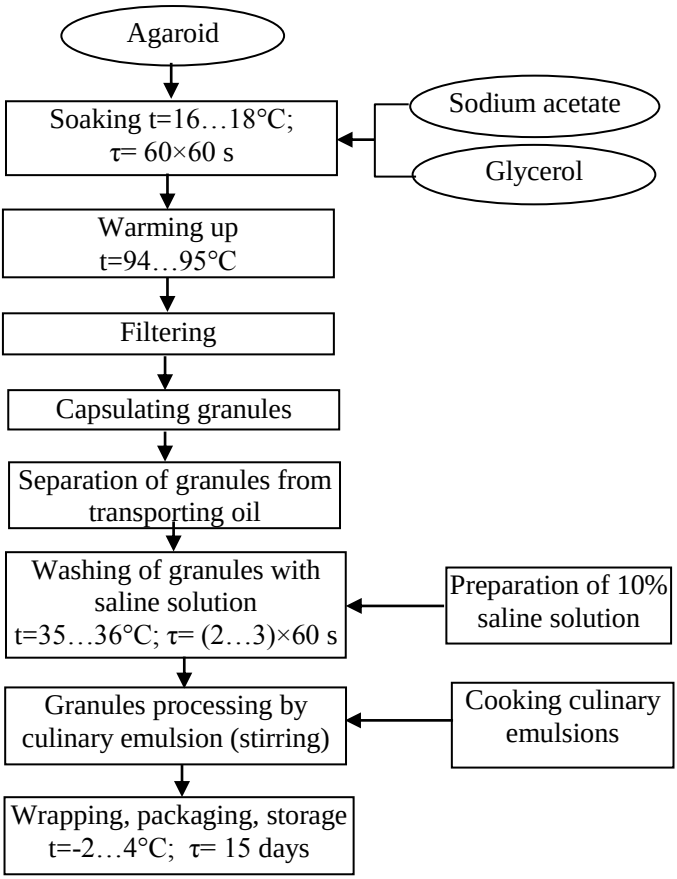


Figure 3.10 - The technological scheme of production of protein red caviar using agaroid for shell preparation

A study of thermal stability at 60 ° C showed that the shell obtained on the basis of a 5% agaroid solution does not withstand this temperature for 60 × 60 s. The shell, which includes modifiers, does not change shape for 180 × 60 s, washed from oil with a 10%

solution of table salt, the shell has a heat resistance of at least 360 × 60 s at a temperature of 60 ° C, this heat resistance guarantees the preservation of integrity and elimination of the appearance of the deformation during storage of the finished product.

The results obtained suggest that only on the basis of agaroid with qualitatively modified properties can be obtained granules shell with the necessary structural and mechanical properties.

In the process of obtaining caviar, mass of the granules varies slightly. After washing with 10% salt solution, the mass increases by only 7 g, and after separation of the solution decreases by 27 g, the weight of the finished product increases by 23.7% due to the emulsion added.

Thus, the studies made it possible to develop a technology of heat-resistant shell for protein red caviar based on agaroid.

In the finished product protein contains about 7%, lipid content reaches 24%, minerals - 2.5%. A caviar shell with the necessary organoleptic and structural-mechanical properties was developed on the basis of an agaroid with qualitatively changed functional properties.

3.4.3 The technological scheme of shell on complex jelly forming agents

The proposed methods of qualitative change of sulfited polysaccharides have allowed to develop a new technology of shell granules analog of caviar of salmon fish species on the basis of complex jellies. It was found that the jelly strength with the joint introduction of salts, as a rule, higher than the introduction of each salt separately. The presence of alcohol in such systems (with two salts) contributes to the increase of mechanical strength of jelly.

The highest strength has jelly with a concentration of sodium chloride in the range of 1 ... 2%. The strength of the jelly, containing 3.5% agaroid, 5% sodium acetate and 0.3% glycerol, corresponds to about 1700 g, maximum the structure is strengthening with the introduction of 1.5% sodium chloride and thus reaches 2125 g, which is 125%. The strength of the jelly containing 5% agaroid, 5% sodium acetate and 0.3% glycerol - 1900 g, thus, the increase in the jelly strength containing 3.5% agaroid, with the addition of table salt, compared with the jelly containing 5% fikokoloid, is 2225 g.

In addition to those previously tested, another modifier was used - $FeCl_3$. Ion III (in the form of iron chloride) makes significant adjustments in the jelly of the agaroid. It is established that the most rational concentration of FeCl3 is 0.1… 0.3%. With this amount of additive strength of the jelly increases from 2300 to 2730 g. Strengthening the structure allows an average of 19% also, as in the previous case, to reduce the expenses of the structure.

The rate of structure formation depends to a large extent on the concentration of the jelly formation agent and the modifiers introduced into the solution. The most advantageous position is agaroid with additives. After (8… 10)×60 s the location of the granules in the forming medium with a temperature of 26 °C shell granules reach a certain desired value - 258 $Pa \times 10^2$. The shell obtained on the basis of complex jelly formation agents - agaroid and agar makers reached the required strength at the same temperature of the forming medium after (10… 12)×60 s, and when using the agaroid and furcellaran the strength for 12×60 s reached only 88 % relative to the strength of the shell prepared on the agar. The results obtained indicate that in order to conduct a stable capsulation process on the basis of complex jelly formation agents (agaroid and furcellaran), the temperature of the oil at which the granule formation takes place should be significantly lower.

Thus, when capsulating granules on the basis of agaroid with additives and complex jellies - agaroid:agar the temperature of the forming medium is at the level of 26 ± 2 °C, and when receiving capsules on the basis of agarid:furcellaran it corresponds to 16 ± 2 °C. From this it follows that in the installation for the production of granules, the process of cooling the oil with a refrigerant, which is fed by a special refrigeration compressor into the shirt, which forms the columns, is excluded.

Thus, in the process of washing with a 10% solution of sodium chloride shell granules, melting temperature of the jelly increases significantly. To a greater extent, this occurs with the shell obtained on the basis of agaroid with additives. The melting temperature of complex fikokoloids also increases, but to a lesser extent.

A study of the heat stability of the granule shell at 80 ° C showed that the capsules were kept at this temperature for (120…

150) × 60 s without losing shape.

The technological scheme of obtaining the shell of red caviar "Yantar" on the basis of complex jelly forming agents is presented in fig. 3.11.

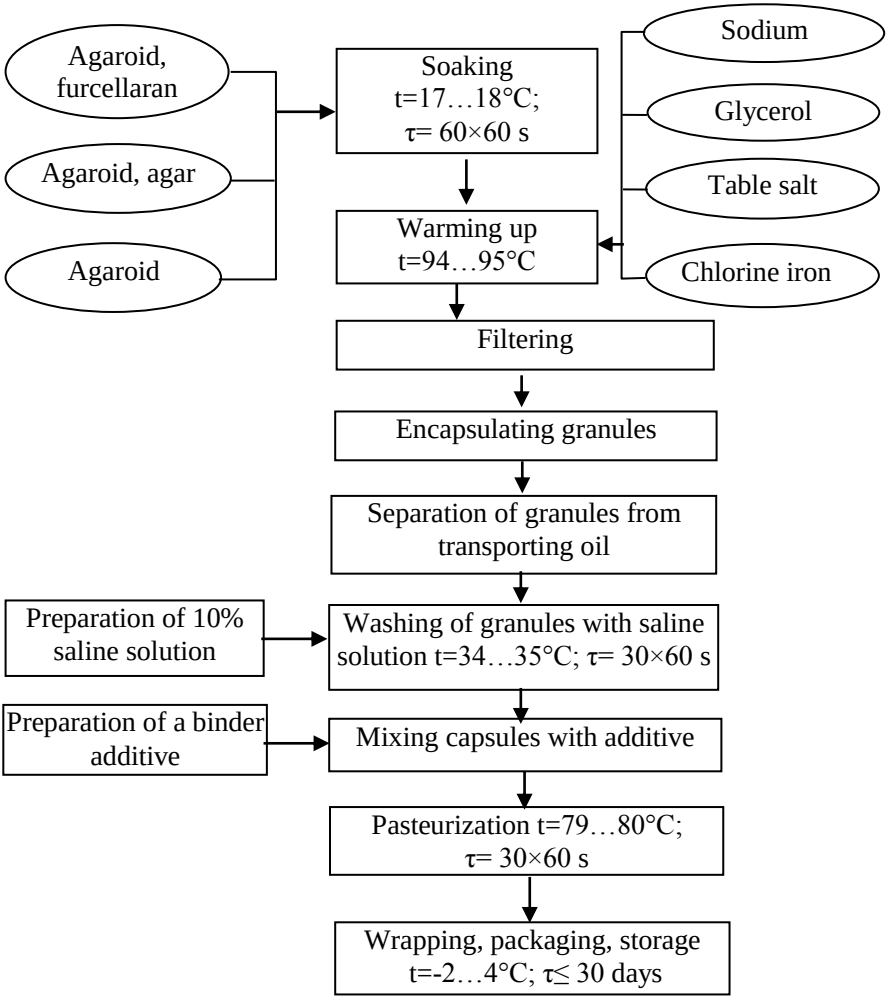


Figure 3.11 - The technological scheme of red caviar "Yantar" using complex jelly forming agents for shell preparation

3.5 Technologies of agar, furcellaran, agaroid jelly forming compositions

Therefore, in the process of obtaining a product, the volume, diameter, weight, thickness of the shell changes slightly. Moreover, these indicators fluctuate depending on the technological stages. Contact granules with water solutions increases volume, diameter and weight. And the complex of researches made it possible to scientifically substantiate and implement on an industrial scale the technological process of obtaining red caviar "Yantar".

The proposed additives are an unconventional raw material for food businesses, they are also used in recipes in small concentrations. Weighing and dosing in real production is a time-consuming process. At the same time, disruption of the optimum ratio of ingredients may reduce the expected effect. In this regard, the level of training of the workforce should be determined. Undoubtedly, it is most rational to produce a structure-forming agent with qualitatively modified functional properties in the form of a dry mixture. For this purpose mix the jelly forming agent, the polyatomic alcohol, the organic acid salt or together the salt of the organic and inorganic acid. The recipe composition of the jelly forming compositions is presented in table. 3.10-3.14. In Fig. 3.12 is a technological scheme for obtaining a jelly forming composition of agar . The sequence of technological operations to obtain the jelly forming composition includes: additional washing of the jelly forming agent before drying; mixing with additives-modifiers, after obtaining a homogeneous mixture; wrapping; packaging.

Table 3.10 - The recipe composition of jelly forming composition of the agar

Name of raw materials	Mass fraction of solids	Raw material consumption per 100 kg, kg	
		in reality	in solids
Agar	85.0	60.5	55.3
Sodium acetate	90.0	4.2	3.8
Mannitol	97.0	36.6	35.2
Total		101.0	94.3
Output		100.0	93.4

Table 3.11 - The recipe composition of jelly forming composition of the furcellaran

Name of raw materials	Mass fraction of solids	Raw material consumption per 100 kg, kg	
		in reality	in solids
Furcellaran	85.0	66.4	56.4
Sodium acetate	90.0	10.9	9.8
Sorbitol	95.0	23.7	22.5
Total		101.0	88.7
Output		100.0	87.8

Table 3.12 - The recipe composition of jelly forming composition of the agaroid

Name of raw materials	Mass fraction of solids	Raw material consumption per 100 kg, kg	
		in reality	in solids
Агароїд	85.0	56.9	48.4
Sodium acetate	90.0	12.1	10.9
Sorbitol	95.0	32.0	30.4
Total		101.0	89.7
Output		100.0	88.8

Table 3.13 - The recipe composition of jelly forming composition of the agaroid

Name of raw materials	Mass fraction of solids	Raw material consumption per 100 kg, kg	
		in reality	in solids
Агароїд	85.0	55.7	47.3
Sodium acetate	90.0	18.6	16.7
Sorbitol	95.0	18.6	17.7
Sodium chloride	90.0	8.1	7.3
Total		101.0	89.0
Output		100.0	88.1

Table 3.14 - The recipe composition of jelly forming composition of the furcellaran

Name of raw materials	Mass fraction of solids	Raw material consumption per 100 kg, kg	
		in reality	in solids
Furcellaran	85.0	64.5	54.8
Sodium acetate	90.0	14.4	13.0
Sorbitol	95.0	14.4	13.7
Sodium chloride	90.0	7.7	6.9
Total		101.0	88.4
Output		100.0	87.5

The technology of obtaining the jelly-forming composition does not require highly specialized and expensive equipment. Mixing of dry components occurs in mixing machines of periodic action. Then the jelly-forming composition is packed in paper bags.

The storage conditions of traditional jelly forming agents can be extended to jelly forming compositions as their humidity is within 15%. Storage is carried out at temperatures not higher than 20 ° C and relative humidity of air not more than 80%.

Thus, the agaroid has a considerable ability to retain oxygen. Jelly-forming compositions enhance this effect in solutions, that is,

synergism of their infusion. This phenomenon can be explained by the formation a viscous membrane on the surface of solutions, which can interfere with the release of oxygen.

Jelly formation in solutions containing only agaroid leads to a decrease in the rate of oxygen output. The formation of a jelly in the presence of acetate or sorbate is accompanied by an increase in the penetration of the membrane with respect to oxygen. This reduces the ability of the system to hold it.

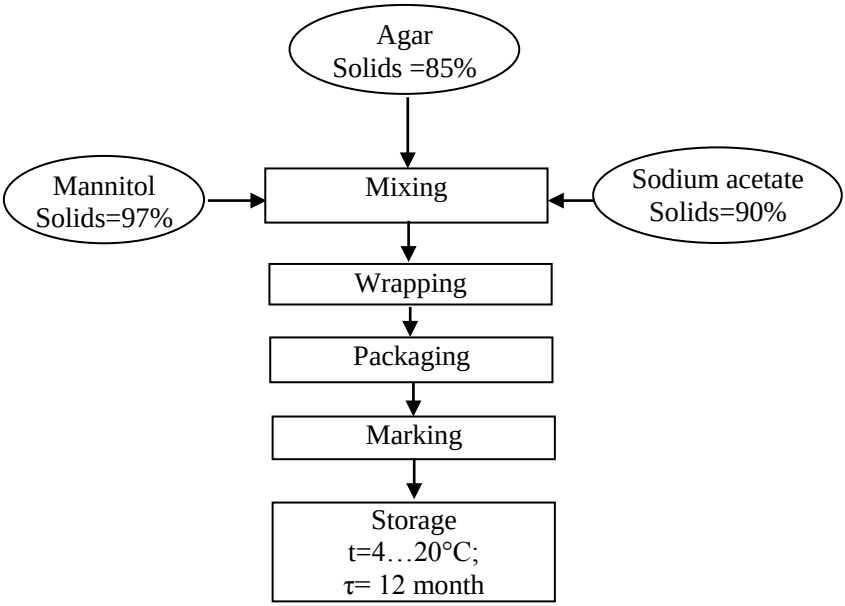


Figure 3.12 – The technological scheme of jelly forming composition

Jellies containing containing together organic acid salts and polyatomic alcohols, the degree of oxygen retention is almost indistinguishable from the control sample.

The data obtained indicate that the introduction of the additive in the jelly forming compositions does not impair the quality of the finished product from a microbiological point of view.

3.5 Technology of heat-resistant frozen fillings

3.5.1 Development of recipe and technology of thermostable filling using dairy raw material and sesame seeds concentrate

In previous studies, it was found that the main recipe components that give thermostable and structural-mechanical properties of TF are hydrocolloids - modified corn starch and low-esterified citrus pectin. These hydrocolloids, together with calcium ions (contained in dairy raw materials and calcium citrate), which "crosslink" pectin molecules to form calcium bridges, are constituent units of a strong spatial grid of filling. It was also found that the addition of sesame seeds concentrate to the filling, has a positive effect on a number of physico-chemical parameters of the product. Thus, the results of the research of analytical, organoleptic, structural-mechanical, a number of physicochemical and technological properties of the experimental system of thermostable filling became the reason for further scientific substantiation of the formulation (Tables 3.1 and 3.2) and technology of production of thermostable filling (Fig. 3.1).

In order to clearly demonstrate the positive effect of sesame seeds concentrate on the quality characteristics of the filling, the results of the experimental studies are further presented in the section with a comparison of the results obtained from studies of the control sample of thermostable filling made without adding the sesame seed concentrate according to the recipe in Table 3.1, and a sample of thermostable filling using dairy raw materials and sesame seeds concentrate (recipe is provided in Table 3.2).

Table 3.1 - Consolidated recipe of thermostable filling per 100 kg

№	Raw materials	Mass fraction of solids, %	Calculation rate per 100 kg filling, kg	
			In reality	In solids
1	White sugar	99.85	35.99	35.94
2	Skimmed milk powder	96.00	14.19	13.63
3	Starch treacle	78.00	5.07	3.65
4	Modified corn starch	88.00	3.04	2.68
5	Refined deodorized sunflower oil	99.90	2.53	2.53
6	Low-esterified citrus pectin	90.00	0.81	0.73
7	Calcium citrate	97.00	0.04	0.04
8	Drinking water	–	41.4	–
Total		-	105.30	59.20
Product yield		56.22	100.00	56.22

Table 3.2- Consolidated recipe of thermostable filling using dairy raw material and sesame seeds concentrate per 100 kg

№	Raw materials	Mass fraction of solids, %	Calculation rate per 100 kg filling, kg	
			In reality	In solids
1	White sugar	99.85	36.00	35.99
2	Skimmed milk powder	96.00	7.90	7.59
3	Sesame seed concentrate	92.00	6.30	5.80
4	Starch treacle	78.00	5.00	3.60
5	Modified corn starch	88.00	3.00	2.64
6	Low-esterified citrus pectin	90.00	0.80	0.72
7	Refined deodorized sunflower oil	99.90	2.10	2.10
8	Calcium citrate	97.00	0.04	0.04
9	Drinking water	–	44.30	–
Total		–	105.30	58.48
Product yield		55,54	100.00	55.54

The technological system of the TF production consists of four logically and functionally interconnected subsystems. In the first stage - preparation of prescription components (subsystem D) is mixed low-esterified pectin citrus with ⅛ a part of sugar and ⅓ a part of drinking water at a temperature of 40…45 °C, carefully mixed and stayed for swelling at (20…24)×60^2 s. The skimmed milk powder is mixed with drinking water at temperatures of 30…35 °C and sustained for (1…3)×60^2 s. The reconstituted milk is pasteurized at 70…74 °C for 15…20 s, cooled to 32…36 °C, added modified corn starch and remaining sugar. For receiving thermostable filling of milk-plant composition with these components is entered a pre-prepared sesame seed concentrate. Further mix is mixed for (10…15 ×60 s. After that is added the refined deodorized sunflower oil and emulsify at a rotating speed of 25±1 s^{-1} at 32…36 °C for (2…3)×60 s.

The second stage is mixing and heat treatment (subsystem C). The prepared pectin mixture is boiled at temperatures in the range of 55…85 °C to a solids content of 25±1.5%, the obtained combined base is added and continue to boil to a mass fraction of solids 46±1.5%, then added the starch treacle and boil to the contents solids 56.5±1.5%. At (2…3)×60 s before the end of the boiling process, a pre-prepared 1% solution of calcium citrate is introduced. A solution of calcium citrate is prepared with the addition of citric acid.

The third stage is spilling and structure formation (subsystem B). The resulting system is stirred and poured into a container for structure formation that occurs within 60±12×60^2 s. The resulting product is then packed.

The fourth stage is to obtain thermostable filling with the use of dairy raw materials and sesame seeds concentrate (subsystem A). Ready TF, regardless of the presence in its composition of sesame seeds concentrate, has the following organoleptic characteristics: appearance and consistency - homogeneous, gentle, in measure of dense; filling color - from white to light yellow; smell - inherent in prescription components; the taste is sweet, inherent in the recipe components used. Storage and realization of TH is carried out in three directions. The first direction is the direct realization of the TF within 36 hours after packing at a temperature of 12±2 °C and a relative humidity of 75±2%. The second direction involves the storage of TF for 15 days at a temperature of 0 ... 4 ºC and a relative humidity of 75±2%. Third direction - freezing - storage of TF at temperatures -

18±2 °C for no more than 4 months with a relative humidity of 94±2%. Thus, the connection sequence of the subsystems has a defined purpose and function (Table 3.3).

Table 3.3-Structure of technological system of TF production

Name of subsystem (stage)	Name of the subsystem and operations	Characteristics functioning of subsystems (stage)
D «Preparation of prescription components»	D_1 «Obtaining a combined basis»: – mixing; – restoration and mixing; – pasteurization; – cooling; – mixing; – emulsification	Quantity and quality control. Ensuring dissolution and swelling.
	D_2 «Obtaining a pectin-sugar mixture»: – siftings; – compound; – mixing; – swelling; – filtering	
C «Mixing and heat treatment»	Heat treatment (boiling)	Compound of prescription components, formation of structural-mechanical and physicochemical properties
	Filtering	
B «Spilling and structure formation»	Spill into molds	Providing the form, structure and necessary qualitative characteristics of TF
	Structure formation	
	Packing	
A «Obtain thermostable filling with the use of dairy raw materials and sesame seeds concentrate»	A_1 «Realization»: – realization	Obtaining TF with specified organoleptic, physicochemical, structural-mechanical and microbiological characteristics (with the possibility of storage in the frozen state)
	A_2 «Short-term storage»: – storage	
	A_3 «Long-term storage»: – freezing; – storage	

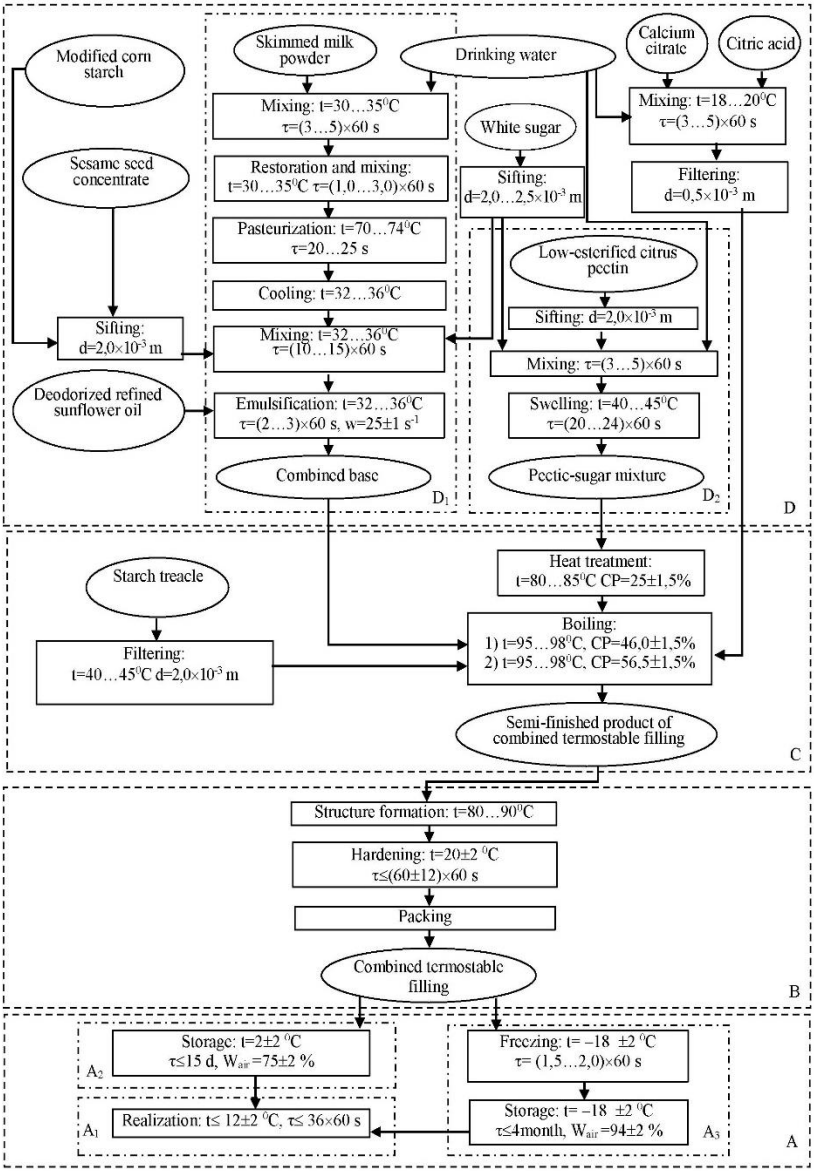


Figure 3.1. Technological scheme of thermostable frozen filling using dairy raw materials and sesame seeds concentrate

3.5.2 Study of microbiological indicators of thermostable filling using dairy raw material and sesame seeds concentrate and justification of its storage life under traditional conditions and frozen

Microbiological indicators are important fundamental indicators of the quality of thermostable fillings, which determine their suitability for consumption. Given that the developed TF contains about 45% moisture, it is a receptive medium for the development of microorganisms. Due to the attraction to the TF formulation the components of protein-polysaccharide nature with high hydrophilic properties and moisture retention, some moisture becomes bound. However, there is a risk of introducing harmful microflora: molds and yeast, so there is a need to study the microbiological parameters of TF (Table 3.4).

Table 3.4-Microbiological indicators of TF

Indicator	TF control sample					Developed TF sample with sesame seed concentrate				
	Freshly made	Storage temperature, °C				Freshly made	Storage temperature, °C			
		2±2		−18±2			2±2		−18±2	
		after 15days	after 28days	after 4 months	after 6 months		after 15days	after 28 days	after 4 months	after 6 months
1	2	3	4	5	6	7	8	9	10	11
Quantity of Mesophilic Aerobic and Facultative Anaerobic Microorganisms (QMAFAM), number of conventional units (NCU) in 1 g not more $1,0\times10^3$	0.5×10^3	0.7×10^3	1.0×10^3	0.9×10^3	1.0×10^3	0.5×10^3	0.75×10^3	1.0×10^3	0.85×10^3	1.0×10^3
E. coli bacteria, in 0.001 g is not allowed	Not detected					Not detected				
Conditionally pathogenic microorganisms, including Staphylococcus aureus, in 0.1 g is not allowed NCU	Not detected					Not detected				

Continuation of Table 3.4

1	2	3	4	5	6	7	8	9	10	11
Pathogenic microorganisms, including Salmonella, in 25 g is not allowed	Not detected					Not detected				
Amount of yeast and mold, in 1 g not more 50 NCU	Not detected					Not detected				

It can be seen from Table 3.4 shows that the microbiological parameters of the samples of TF - freshly made and the samples stored at 2±2 °C for 15 days - do not exceed the norms [106]. The final norm of QMAFAM $1{,}0\times10^3$ NCU in 1 g reaches the samples after 28 days of storage at the same temperature and after 6 months of storage at a temperature of -18±2 °C. Therefore, it is advisable to use low temperatures to prevent unwanted changes and preserve the quality characteristics of development.

Thus, according to the results of TF microbiological studies, the recommended shelf life at 2±2 °C is 15 days, and at temperatures of –18±2 °C - 4 months. Taking into account this results, it is advisable to submit the results of further experimental studies under the established rational storage conditions, under which the proposed thermostable fillings meets the microbiological norms of the current medical and biological requirements and sanitary quality standards. [106].

3.5.3 Study of the chemical composition of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

The thermostable filling is a complex system consisting of a certain number of components of a particular nutritional and biological value. During the development of the TF formulation composition it was guided by the promising direction of creating a combined product of high biological value with specified thermostable, structural, mechanical and physico-chemical characteristics. This was achieved by the joint use of hydrocolloids of different nature and the introduction into the TF formulation of

protein plant product - sesame seed concentrate [123; 159]. That is why, in order to understand the biological and nutritional value of TF, it is necessary to present a series of studies on the chemical composition of scientific development. General characteristics of the TF chemical composition are given in Table 3.5.

Table 3.5- Characterization of the TF chemical composition

Name of component	Contents, %					
	TF control sample			Developed TF sample with sesame seed concentrate		
	Freshly made	Storage temperature, °C		Freshly made	Storage temperature, °C	
		2 ± 2 after 15 days	–18 ± 2 after 4 months		2 ± 2 after 15 days	–18 ± 2 after 4 months
Proteins	5.00±0.25	5.00±0.25	5.08±0.25	5.10±0.26	5.10±0.26	5.16±0.26
Fats	2.53±0.13	2.55±0.13	2.62±0.13	2.48±0.10	2.50±0.10	2.58±0.10
Carbohydrates	45.63±2.30	45.63±2.30	45.63±2.30	41.35±2.10	41.35±2.10	41.35±2.10
Dietary fiber	0.95±0.03	0.95±0.03	0.95±0.03	0.95±0.03	0.95±0.03	0.95±0.03
Moisture	42.30±2.00	41.40±2.00	40.00±2.00	45.30±2.20	44.30±2.20	42.00±2.10

From the data Table 3.5 shows that the nutrients of both freshly made samples of TF remain at almost the same level after storage under traditional conditions for 15 days (slightly reduced moisture). The total amount of proteins, fats and carbohydrates at a storage temperature of 2±2 °C of the TF control sample is 5.00, 2.55 and 45.63%, respectively, and the developed TF sample with the addition of sesame seeds concentrate, respectively 5.10, 2.50 and 41.35%. It was found that the total number of dietary fiber under different regimes and the duration of storage of these samples remains unchanged - 0.95%.

Experimental studies have shown that a number of physico-chemical and biochemical processes undergo the filling of changes during storage. In particular, during freezing due to moisture crystallization, it is possible to damage protein and polysaccharide molecules by large ice crystals, accompanied by moisture loss. This is confirmed by the results of the moisture change (Table 3.5): according to the results of the chemical composition evaluation of the developed samples at a storage temperature of -18±2 °C, the total amount of proteins and fats increases, and moisture - decreases relative to the samples stored at a temperature of 2±2 °C 15 days.

Therefore, due to the loss of moisture by the control and developed samples of TF with a plant protein supplement (respectively 3.4 and 5.2%) after their defrosting, the amount of protein substances is concentrated, which is accompanied by an increase of proteins by 1.6 and 1.2%, respectively. The total fat content in these samples increases respectively by 2.7 and 3.2%. It is likely that the increase in fat content after defrosting is due to oxidation and hydrolysis processes [31; 129; 131; 147]. Thus, freezing contributes to a slight loss of moisture with a parallel increase (concentration) of nutrients.

Since a certain amount of protein in the developed filling is caused by the use of plant protein-containing raw material - sesame seed concentrate, it is necessary to provide a comparative characteristic of the amino acid content of the sesame seeds and directly in its concentrate (Table 3.6).

Table 3.6 - Comparative characteristics of the amino acid composition of the raw material

The name of the component	Contents, %	
	Sesame seeds	Sesame seed concentrate
Water	9.00	8.00
Protein	19.40	45.00
Essential amino acids		
Valine	1.20±0.06	2.78±0.10
Isoleucine	0.90±0.05	2.09±0.10
Leucine	1.60±0.08	3.71±0.20
Lysine	0.67±0.03	1.55±0.08
Methionine	0.70±0.04	1.62±0.08
Threonine	0.87±0.04	2.02±0.10
Tryptophan	0.47±0.02	1.09±0.05
Phenylalanine	1.10±0.06	2.55±0.20
Total	7.51±0.38	17.41±0.81
Non essential amino acids		
Alanine	1.10±0.06	2.55±0.10
Aspartic acid	1.90±0.01	4.41±0.22
Histidine	0.60±0.03	1.39±0.07
Glycine	1.20±0.06	2.78±0.10
Glutamic acid	4.70±0.24	10.90±0.5
Proline	0.97±0.05	2.25±0.10
Serine	1.10±0.06	2.55±0.10
Tyrosine	0.87±0.04	2.02±0.10
Cysteine	0.44±0.02	1.02±0.05
Total	12.88±0.7	29.87±1.34

It was found (Table 3.6) that the total content of essential and non essential amino acids for sesame seeds is 7.51 and 12.88% respectively, and for sesame seeds concentrate - 17.41 and 29.87%. That is, a tendency to increase the content of amino acids by 131.82 and 131.91% respectively, relative to the content of sesame seeds.

For a more complete presentation of the biological value of seeds and sesame seeds concentrate, their amino acid score is presented. (Table 3.7). The most significant indicators of the biological value of the protein were established by the calculation method: by calculating the amino acid score, net protein utilization (NPU), protein quality index (Ipq) and biological value (BV).

Table 3.7 - Characterization of biological value of sesame proteins

Name of amino acids	Scale of FAO/WHO, mg/g	Sesame seeds		Sesame seed concentrate	
		Content, mg/g	Score,%	Content, mg/g	Score,%
Isoleucine	40	46.39	115.98	46.44	116.11
Leucine	70	82.47	117.82	82.44	117.78
Lysine	55	34.54	62.79	34.44	62.63
Methionine	35	36.08	103.09	36.00	102.86
Phenylalanine	60	56.70	94.50	56.67	94.44
Threonine	40	44.85	112.11	44.89	112.22
Tryptophan	10	24.23	242.27	24.72	242.22
Valine	50	61.86	123.71	61.78	123.56
NPU	–	0.97		0.97	
BV,%	–	67.89		67.86	
Ipq	–	0.37		0.37	

From the given data in Table 3.7. it was found that the protein of seeds and sesame concentrate is not complete, because there are amino acids in which the value is less than 100%; such amino acids are methionine and phenylalanine. However, the net protein utilization and protein quality index for both samples are 0.97 and 0.37. The biological value for sesame seeds is 67.89% and for sesame seeds concentrate is 67.86%.

Solving the perspective task of creating a product of high biological value, it is advisable to present the characteristics of the amino acid composition of the proposed TF samples under the established TF storage conditions in three possible directions (Table 3.8).

Table 3.8 - Characterization of the amino acid composition of TF

The name of the component	Contents, %					
	TF control sample			Developed TF sample with sesame seed concentrate		
	Freshly made	Storage temperature, °C		Freshly made	Storage temperature, °C	
		2±2	–18±2		2±2	–18±2
		after 15 days	after 4 months		after 15 days	after 4 months
Protein	5.00±0.25	5.00±0.25	5.08±0.25	5.10±0.26	5.10±0.26	5.16±0.26
Essential amino acids						
Valine	0.29±0.01	0.29±0.01	0.27±0.01	0.31±0.02	0.31±0.02	0.30±0.02
Histidine	0.12±0.006	0.12±0.006	0.14±0.007	0.14±0.007	0.14±0.007	0.15±0.007
Isoleucine	0.26±0.01	0.26±0.01	0.25±0.01	0.26±0.08	0.26±0.08	0.24±0.07
Leucine	0.43±0.02	0.43±0.02	0.45±0,02	0.44±0.01	0.44±0.01	0.47±0.01
Lysine	0.34±0.01	0.34±0.01	0.29±0.01	0.28±0.01	0.28±0.01	0.23±0.01
Methionine	0.11±0.006	0.11±0.006	0.09±0.005	0.15±0.008	0.15±0.008	0.14±0.007
Threonine	0.19±0.009	0.19±0.009	0.24±0.01	0.22±0.01	0.22±0.01	0.26±0.01
Tryptophan	0.06±0.003	0.06±0.003	0.08±0.004	0.09±0.005	0.09±0.005	0.1±0.005
Phenylalanine	0.23±0.01	0.22±0.01	0.20±0.01	0.26±0.01	0,26±0,01	0.24±0.01
Total	2.02±0.08	2.02±0.08	2.01±0.09	2.15±0.16	2,15±0,16	2.13±0.15
Non essential amino acids						
Alanine	0.15±0.008	0.15±0.008	0.18±0.009	0.22±0.01	0.22±0.01	0.24±0.01
Asparagine	0.32±0.02	0.34±0.02	0.37±0.02	0.43±0.02	0.43±0.02	0.45±0.02
Glycine	0.09±0.005	0.09±0.005	0.12±0.006	0.20±0.01	0,20±0.01	0.22±0.01
Glutamic acid	0.95±0.05	0.9±0.05	1.04±0.05	1.09±0.05	1.09±0.05	1.15±0.06
Proline	0.42±0.02	0.42±0.02	0.45±0.02	0.35±0.02	0.35±0.02	0.40±0.02
Serine	0.26±0.01	0.24±0.01	0.26±0.01	0.27±0.02	0.27±0.02	0.31±0.02
Tyrosine	0.22±0.01	0.22±0.01	0.25±0.01	0.23±0.01	0.23±0.01	0.26±0.01
Cysteine	0.039±0.001	0.038±0.001	0.02±0.001	0.08±0.004	0.08±0.004	0.07±0.004
Total	2.40±0.12	2.39±0.12	2.69±0.13	2.87±0.14	2.87±0.14	3.10±0.15

It can be seen from Table 3.8 that the amino acid composition of the corresponding freshly made samples of TF and those samples that were stored for 15 days at 2±2 °C, has close values. However, these samples have differences in amino acid

composition when stored at 2±2 °C for 15 days and –18±2 °C for 4 months. It should also be noted higher content of valine, histidine, leucine, threonine, phenylalanine, alanine, asparagine, glutamine and cystine in TF with sesame seed concentrate than in control TF.

Of course, the biological value of a protein depends not only on the number of essential amino acids, but also on their ratio to the reference protein: the greater their difference, the lower the balance and biological value [88; 137; 156]. The biological value is given for samples of TF, which were stored under the specified storage conditions in Table 3.9.

Table 3.9 - Characterization of biological value of TF proteins

Name of amino acids	Scale of FAO/WHO, mg/g	TF control sample				Developed TF sample with sesame seed concentrate			
		Storage temperature, °C				Storage temperature, °C			
		2±2		–18±2		2±2		–18±2	
		after 15 days		after 4 months		after 15 days		after 4 months	
		Content mg/g	Score, %	Content mg/g	Score, %	Content mg/g	Score, %	Content mg/g	Score, %
1	2	3	4	5	6	7	8	9	10
Isoleucine	40	52.00	130.00	49.21	123.03	50.98	127.45	46.51	116.28
Leucine	70	86.00	122.86	88.58	126.55	86.27	123.25	91.09	130.12
Lysine	55	68.00	123.64	57.09	103.79	54.90	99.82	44.57	81.04
Methionine +cysteine	35	22.00	62.86	17.72	50.62	29.41	84.03	27.13	77.52
Phenylalanine+ tyrosine	60	88.00	146.67	88.58	147.64	96.08	160.13	96.90	161.50
Threonine	40	38.00	95.00	47.24	118.11	43.14	107.84	50.39	125.97
Tryptophan	10	12.00	120.00	15.75	157.48	17.65	176.47	19.38	193.80
Valine	50	58.00	116.00	53.15	106.30	60.78	121.57	58.14	116.28
NPU	–	0.56		0.46		0.82		0.76	
BV,%	–	62.86		61.33		65.50		64.69	
Ipq	–	0.39		0.39		0.36		0.36	

According to the Table 3.9 it is established that all the proposed samples of TF have the lowest value of amino acid score in the ratio of methionine + cystine amino acids. Net protein utilization, biological value and protein quality index of TF control samples, stored under traditional conditions and frozen are 0.56, 62.86%, 0.39 and 0.46, 61.33%, 0, 39, respectively. The same indicators under the

same storage conditions of TF samples with sesame seed concentrate are as follows: 0.82, 65.50%, 0.36 and 0.76, 64.69%, 0.36.

The following studies are devoted to the determination of fatty acid composition of scientific development (Table 3.10).

Table 3.10 - Comparative characteristics of fatty acid composition of raw materials

Name of fatty acid	Content,% per 100 g	
	Sesame seeds	Sesame seed concentrate
Saturated		
Myristic acid $C_{14:0}$	0.12±0.004	0.001±0.00003
Palmitic acid $C_{16:0}$	4.44±0.22	0.36±0.02
Stearic acid $C_{18:0}$	2.09±0.10	0.17±0.009
Total, %	6.65±0.32	0.53±0.03
Unsaturated		
Palmitoleic acid $C_{16:1}$	0.15±0.008	0.01±0.0003
Oleic acid $C_{18:1}$	18.50±0.93	1.48±0.07
Linoleic acid $C_{18:2}$	21.37±1.1	1.70±0.09
Linolenic acid $C_{18:3}$	0.38±0.02	0.03±0.002
Total, %	40.40 ±2.06	3.22±0.17

According to the Table 3.10 there is a decrease in the total amount of fatty acids in the sesame seed concentrate: the total amount of saturated and unsaturated fatty acids for sesame seeds is 6.65 and 40.40% respectively , and the sesame seed concentrate is 0.53 and 3.22%.

In view of the destructive processes, the results of the study of the TF fatty acid composition were determined under the established storage conditions of the filling in three possible directions (Table 3.11). Studies of the fatty acids content of the TF proposed samples indicate a predominantly increased their content in the samples of the fillings with a sesame seeds concentrate. Such an increase is likely due to the chemical composition of the plant protein supplement and the partial replacement of non-fat dairy raw materials with concentrate.

Table 3.11 - Characteristics of fatty acid composition of TF

Name of fatty acid	Content,% per 100 g					
	TF control sample			Developed TF sample with sesame seed concentrate		
	Freshly made	Storage temperature, °C		Freshly made	Storage temperature, °C	
		2±2	–18±2		2±2	–18±2
		after 15 days	after 4 months		after 15 days	after 4 months
Saturated						
Myristic acid $C_{14:0}$	0.0088± 0.0004	0.009± 0.0005	0.012± 0.0006	0.009± 0.0004	0.01± 0.0005	0.015± 0.0008
Palmitic acid $C_{16:0}$	0.02±0.001	0.02±0.001	0.03±0.001	0.22±0.01	0.25±0.01	0.30±0.02
Stearic acid $C_{18:0}$	0.01±0.0005	0.03±0.0001	0.1±0.005	0.10±0.005	0.12±0.006	0.22±0.01
Total, %	0.039±0.002	0.059±0.001	0.14±0.007	0.33±0.015	0.38±0.017	0.54±0.031
Unsaturated						
Palmitoleic acid $C_{16:1}$	0.004± 0.0002	0.003± 0.0001	0.001± 0.00005	0.01± 0.0005	0.007± 0.0003	0.003± 0.0001
Oleic acid $C_{18:1}$	0.02± 0.001	0.02± 0.001	0.015± 0.0007	2.58±0.13	2.55±0.13	2.48±0.12
Linoleic acid $C_{18:2}$	0.003± 0.0001	0.003± 0.0001	0.002± 0.0001	1.62±0.08	1.60±0.08	1.60±0.08
Linolenic acid $C_{18:3}$	0.1±0.005	0.1±0.005	0.05±0.002	0.03±0.002	0.02±0.001	0.02±0.001
Total, %	0.127± 0.006	0.126± 0.068	0.068± 0.003	4.24±0.20	4.18±0.20	4.10±0.20

Table 3.12 - Characteristics of the vitamin composition of TF

Name of vitamin	Content, mg/100 g	
	TF control sample	Developed TF sample with sesame seed concentrate
1	2	3
Water-soluble		
PP (nicotinic acid))	0.93±0.05	1.02±0.05
B_1 (thiamine)	0.04 ±0.002	0.18 ±0.009

Continuation of Table 3.12

1	2	3
B_2 (riboflavin)	0.22±0.01	0.17±0.009
B_5 (pantothenic acid)	0.06 ±0.002	0.03±0.001
B_6 (pyridoxine)	0.052±0.002	0.003±0.0001
B_9 (folic acid)	$(0.62\pm0.03)\cdot10^{-3}$	$(0.34\pm0.02)\cdot10^{-3}$
B_{12} (cyanocobalamin)	$(0.05\pm0.002)\cdot10^{-3}$	$(0.03\pm0.002)\cdot10^{-3}$
C (ascorbic acid)	0.48±0.024	0.27±0.01
H (biotin)	$(0.,40\pm0.02)\cdot10^{-3}$	$(0.22\pm0.01)\cdot10^{-3}$
Total	1.78±0.09	1.67±0.08
Fat-soluble		
D (calciferol)	$(0.0062\pm0.0003)\cdot10^{-3}$	$(0.034\pm0.002)\cdot10^{-3}$
E (tocopherol)	0.98±0.05	0.84±0.04
K (phylloquinone)	–	$(0.57\pm0.03)\cdot10^{-3}$
Total	0.98±0.05	0.84±0.04

The results of determining the vitamin composition (Table 3.12) indicate that the use of sesame seeds concentrate in the technology of TF promotes the appearance of vitamin K, increase the content of vitamin D, but the total amount of fat-soluble vitamins is reduced and for the control sample is 0.98 mg / 100 g, and for sample with concentrate - 0,84 mg / 100 g. The content of water-soluble vitamins in TF with sesame seed concentrate is less than the control sample, and is respectively 1,67 and 1,78 mg / 100 g.

No less valuable for human health are minerals. They significantly affect the structural characteristics of the products, which is caused by their interaction with the polysaccharide molecules [138]. In order to identify and find out their quantity, the characteristics of the mineral composition of the scientific development are given (Table 3.13).

Table 3.13 - Characteristics of the mineral composition of TF

The name of the element	Content, mg/100 g	
	TF control sample	Developed TF sample with sesame seed concentrate
1	2	3
Macroelements		
Calcium	150.90±7.54	263.45±13.20
Magnesium	19.58±0.98	86.25±2.50
Sodium	59.24±2.96	68.60±2.00

Continuation of Table 3.13

1	2	3
Potassium	145.98±7.29	207.96±10.40
Phosphorus	110.08±5.50	199.86±10.00
Chloride	12.81±0.64	12.81±0.40
Total	498.59±25.21	838.88±38.50
Microelements		
Iron	0.28±0.01	2.27±0.1
Zinc	0.05±0.002	0.05±0.002
Iodine	$(1.05\pm0.06)\cdot10^{-3}$	$(0.1\pm0.003)\cdot10^{-3}$
Copper	$(1.4\pm0.07)\cdot10^{-3}$	$(1.4\pm0.07)\cdot10^{-3}$
Manganese	$(0.7\pm0.02)\cdot10^{-3}$	$(0.7\pm0.02)\cdot10^{-3}$
Selenium	0.23±0.01	0.23±0.01
Fluorine	$(2.33\pm0.12)\cdot10^{-3}$	$(2.0\pm0.08)\cdot10^{-3}$
Total	0.56±0.02	2.55±0.11

Table 3.13 shows that the content of minerals in the TF sample with the addition of sesame seeds concentrate relative to the control sample is increased about twice, in particular, a significant increase in the content of calcium, magnesium, potassium, phosphorus and iron.

Drawing general conclusions about the chemical composition of TF, we can note the positive effect of sesame seed concentrate on the biological value of the developed products, vitamin and mineral composition.

3.5.4 Study of physicochemical properties of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

3.5.4.1 Study of chemical changes

Chemical and biochemical processes play a major role in TF technology: they affect product readiness and shelf life. During storage, the filling undergoes a series of transformations that occur under the influence of oxidation processes. The product changes its acidity, which directly affects its organoleptic properties. In view of this, studies to determine the pH (active acidity) of TF are relevant (Fig. 3.2).

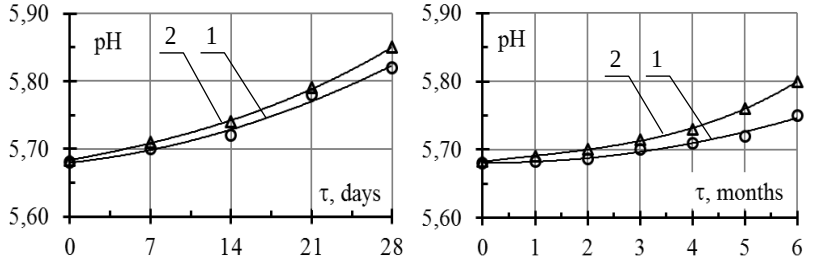


Figure 3.2. Dependence of the TF active acidity on the storage duration at temperature: a) 2±2 °C; b) -18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seed concentrate

In Fig. 3.2 shows that under different storage conditions there is an increase in the active acidity in the test samples of TF, and the presence of a sesame seed concentrate in the recipe composition of TF promotes an increase in the active acidity of the product. This is probably due to the tendency of the plant protein supplement itself to oxidize due to the presence of approximately 10% fat in the concentrate.

As shown in Fig. 3.2 (a), in TF samples, stored at 2±2 °C, a steady increase in active acidity was observed during the first 14 days. Then the rate increased rapidly enough, which may indicate food unsuitability of a product. In Fig. 3.2 b) it is seen that the active acidity of the TF control samples and the samples of the filling with sesame seed concentrate increased steadily during the first 4 months of low temperature storage. After 4 months, the active acidity of both fillings changed more intensively.

Considering the results of the active acidity study of the proposed TF samples under different storage conditions, the following rational storage periods can be recommended: at 2±2 °C for 14 days and at –18±2 °C for 4 months. It is worth noting that the recommended shelf life, taking into account changes in active acidity, does not contradict previous studies.

3.5.4.2 Study of changes in moisture connection forms

3.5.4.2.1 Study of moisture-holding ability

An important criterion for the quality of TF is the ability of the prescription components to retain moisture throughout the shelf life. This property helps to reduce technological costs and allows to obtain a filling with a gel-like gentle and plastic consistency [237; 257; 262; 272; 273; 284]. Therefore, there was a need to investigate the moisture-holding ability of TF. In Fig. 3.3. shows changes in the MHA index of TF under different storage conditions.

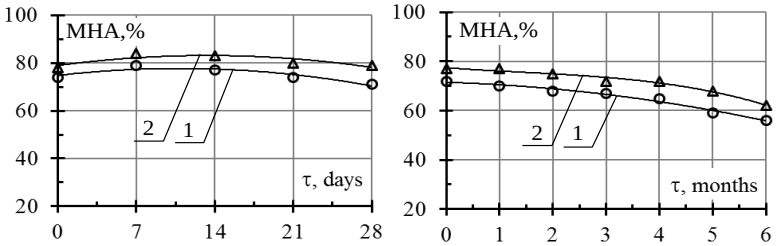


Figure 3.3. Dependence of moisture-holding ability of TF on the storage duration at temperature: a) 2±2 °C; b) –18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seed concentrate

In Fig. 3.3 it is shown that sesame seed concentrate as a prescription ingredient of TF promotes higher MHA of the development. The trends of MHA change in both samples are similar. It is probable that the increase of MHA in the presence of sesame seed concentrate in the system is due to the additional ability to hydratation of plant proteins and polysaccharides, which was established by previous studies of the functional and technological properties of plant protein additives. A decrease of MHA indicates a decrease in the strength of the intermolecular interactions of the formulation components and the release of moisture, which is more relevant after defrosting of the samples when the product structure is "traumatized" by ice crystals [16; 31; 67; 135; 222].

3.5.4.2.2 Determination of changes in product humidity relative to the time of high temperature action

The different nature and chemical composition of the formulation ingredients of TF affect on the content and ratio of free and bound moisture. As it is found that MHA of TF decreases during

storage, it becomes necessary to determine how much moisture is associated with the ingredients of filling . It is known that the weaker the bound moisture, the more intense the spoilage process in the product occur. Free moisture is easily removed by drying. It should also be noted that as the temperature rises, the water molecules move randomly, resulting in a break in hydrogen bond [267].

Moisture content was determined by thermogravimetric method with the help of scales-hydrometers at a constant temperature of 160 °C (Fig. 3.4 та 3.5).

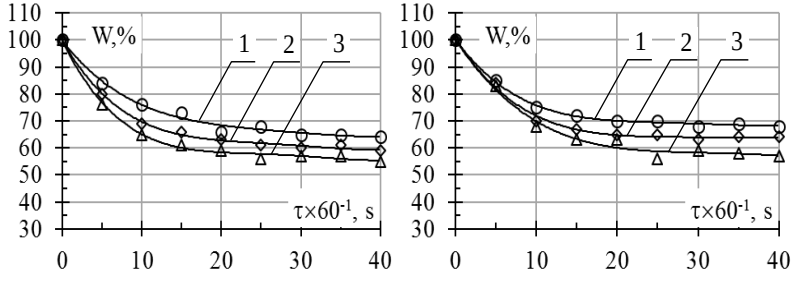


Figure 3.4. Humidity dependence of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature 2±2 °C on duration of high-temperature processing: 1 - freshly made sample; 2 - sample after 14 days of storage; 3 - sample after 28 days of storage

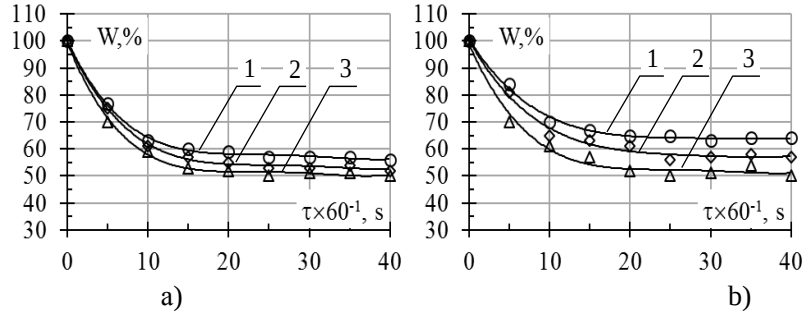


Figure 3.5. Humidity dependence of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature –18±2°C on duration of high-temperature processing: 1 - freshly made sample; 2 - sample after 3 months of storage; 3 - sample after 6 months of storage

For TF is characteristic that its control samples are faster reaching constant humidity than those with sesame seeds concentrate, that is, they are dried more quickly. This tendency is true for TF samples which stored under traditional conditions and for the filling samples that have been frozen (Figs. 3.4 and 3.5). Thus, it has been found that plant protein supplement promotes moisture retention. With regard to freezing, it has a negative effect on the TF structure: TF samples after defrosting are dried faster than similar samples stored under traditional conditions.

It was also found that for TF, which stored under two different conditions, storage adversely affected the ability to hold moisture. With regard to changes in the humidity of TF, depending on the time of high temperature action, the following can be stated. First, it was found that the presence of sesame seeds concentrate slows the removal of free moisture. Secondly, it can be seen that the longer the product is stored under traditional conditions and at low temperatures, the more free moisture it has. And freezing leads to destruction of the structure [16; 31; 67; 135; 222]. Studies conducted to study the changes in humidity of TF depending on the time of high temperature action confirm the data obtained from the study of MHA.

3.5.4.2.3 Determination of moisture condition

A characteristic feature of free moisture is not only its ability to act as a solvent, but also its inherent high mobility, which can be determined by spin echo method - nuclear magnetic resonance [27; 30; 149; 173; 222; 245]. During the study, particular attention was paid to the chemical composition of TF samples, since the chemical composition affects the rate of energy redistribution in the spin-spin system and is characterized by spin-spin interaction and molecular mobility of water. It should be noted that the spin-spin relaxation time (T_2) depends on the mobility of the protons that make up the water molecule; the length T_2 increases with the mobility of protons.

Also, the temperature modes of storage have a great influence on the change in the moisture state. Thus, control TF and TF with sesame seed concentrate were stored under two temperature conditions studied:

under traditional conditions (2±2 °C) for 28 days and in a frozen state (-18±2 °C) for 6 months. Figure 3.6 (b) shows the effect of freezing on the change in spin-spin relaxation which characterizing the molecular mobility of moisture, thereby indicating the free moisture in the TF samples with different content of dairy and plant components during low-temperature storage.

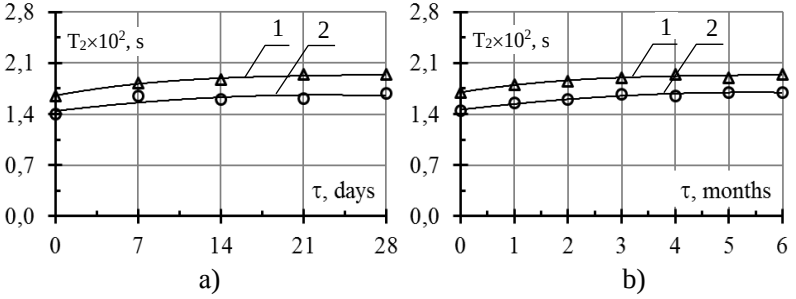


Figure 3.6. Dependence of spin-spin relaxation time (T_2) of TF on the duration of storage at temperature a) 2±2 °C and b) –18±2 °C: 1 - TF control sample; 2 - developed TF sample with sesame seed concentrate

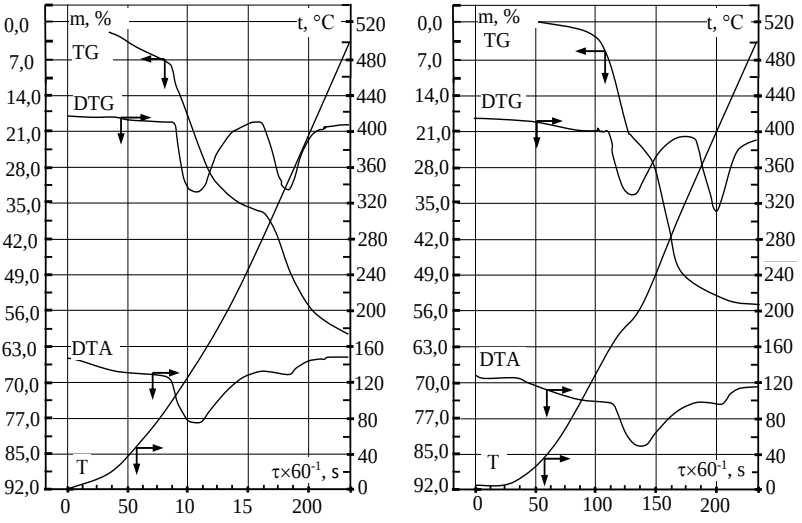
The results of the studies presented in Fig. 4.6, indicate that at storage temperatures of 2±2 °C and –18±2 °C of the TF samples, the spin-spin relaxation time (T_2) increases in the TF control relative to TF with the sesame seed concentrate. Thus, for a freshly made TF control sample (Fig. 3.6 a) and after 28 days of storage at a temperature of 2±2 °C T_2 changes from 0.0171 to 0.0194 s, and for the developed TF sample with concentrate - from 0.0147 to 0.0170 s.

Freezing does not significantly affect the change in relaxation time. In the study of spin-spin relaxation of the dipoles of water of TF, it is found that the time of spin-spin relaxation of TF increases during storage, which indicates the loosening of the structure and the release of free moisture. Freezing does not significantly affect the time of spin-spin relaxation. The lowest values of T_2 are inherent in TF with sesame seed concentrate. This confirms the growth of MHA in the filling with sesame seeds concentrate, as noted above.

3.5.4.2.4 Study of kinetic regimes of endothermic processes

Previous research has shown that by using in the TF formulation of sesame seed concentrate, low-esterified citrus pectin and modified corn starch, bound moisture prevails. Bound moisture, unlike free moisture, is characterized by difficulty in removal, since it requires a high temperature, accompanied by absorption (endothermic conversion) or allocation of heat (exothermic conversion). Thus, physico-chemical changes in the TF occur, in particular changes of mass during the action of temperature.

The kinetic parameters of endothermic processes in TF were investigated using differential thermal analysis (DTA) on a derivatograph. The essence of the method is the assumption that at given the constant rate of heating, the value of the mass change degree or heat absorption by the system in the region of fixed onset and maximum process development is proportional to the conversion rate constant for each temperature value. Moisture bonding patterns were determined by analyzing the curves of change in mass (TG), differential thermogravimetry (DTG and DTA) and temperature (T) [152] (Figs. 3.7 and 3.8).



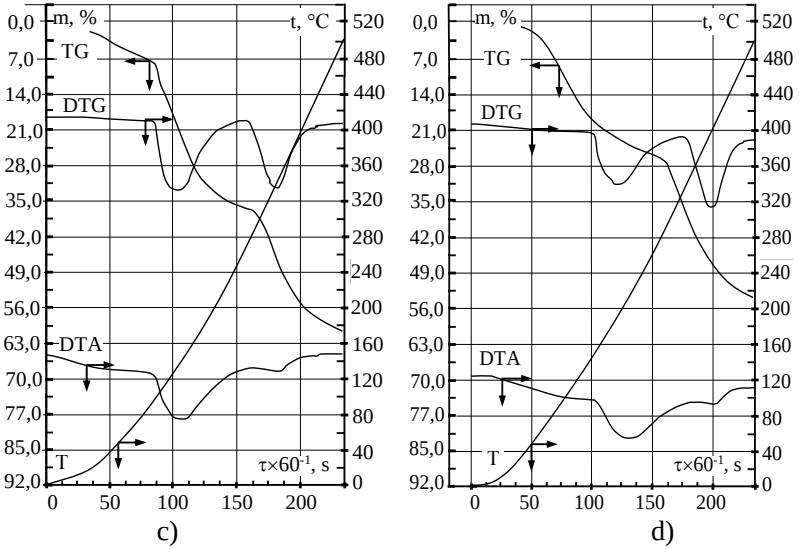
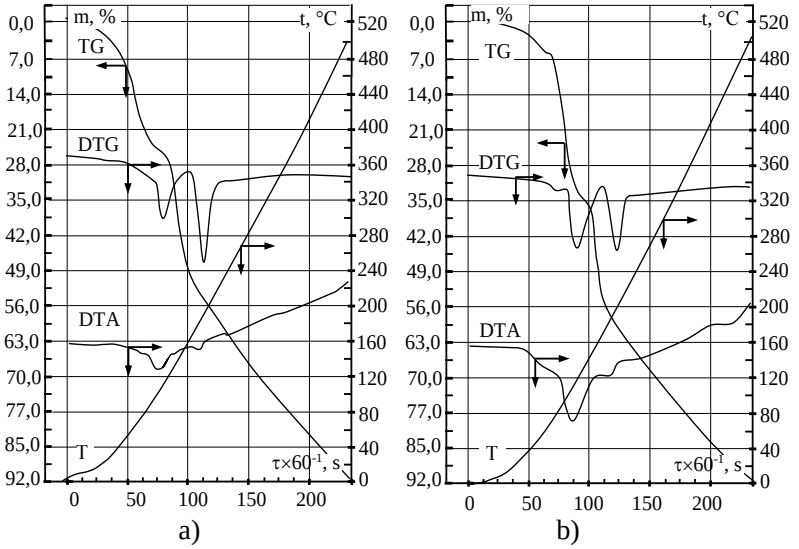


Fig. 3.7. Studying of endothermic processes kinetic parameters of TF control sample: a) freshly made; b) after 15 days of storage at 2±2 °C; c) freshly made defrozen; d) after 4 months of storage at a temperature of −18±2 °C



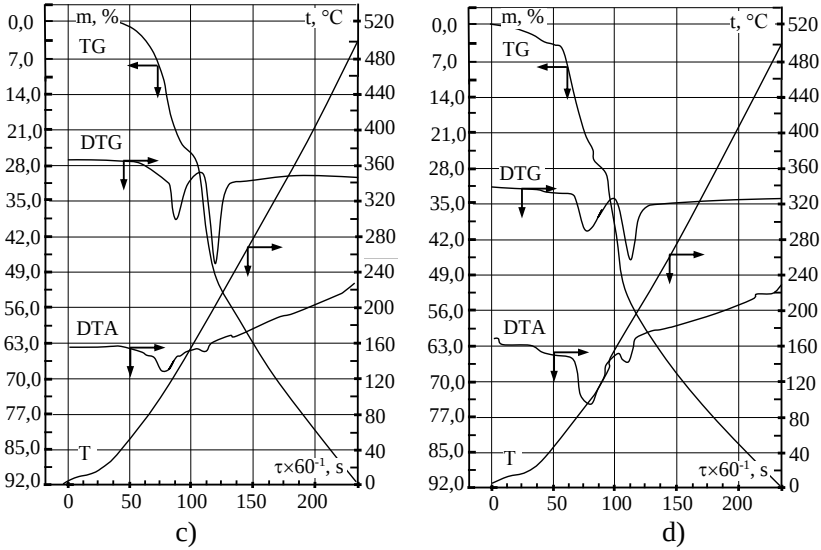


Fig. 3.8. Studying of endothermic processes kinetic parameters of TF with sesame seed concentrate: a) freshly made; b) after 15 days of storage at 2±2 °C; c) freshly made defrozen; d) after 4 months storage at −18±2 °C

In Fig. 3.7 and 3.8 show different dynamics of moisture loss with increasing temperature influence on TF, which indicates about different forms of moisture connexion in it. Thus, according to the experimental DTG curves indicating the amount of moisture loss (TG) under a given temperature influence (T), three peaks of the endothermic process of mass removal of moisture from the TF were recorded. The maximums (peaks) of moisture mass loss at temperature in the TF, which determine the origin of the bond and characterize the moisture bond form are given in Table. 3.14.

Table 3.14 - Characterization of maxima of TF mass loss

TF sample		Temperature maximum, °C	The amount of moisture released			
			Free		Bound	
			%	mg	%	mg
1	2	3	4	5	6	7
TF control	Freshly made	I stage				
		100±2	6.0±0.5	30.0±0.5	–	–
		II stage				
		120±2	–	–	16.0±0.5	80.0±0.5
		173±2	–	–	30.0±0.5	150.0±0.5
		206±2	–	–	41.0±0.5	205.0±0.5
		III stage				
		235±2	–	–	53.0±0.5	265.0±0.5
	Freshly made (defrozen)	I stage				
		100±2	6,5±0,5	32,5±0,5	–	–
		II stage				
		120±2	–	–	23.0±0.5	115.0±0.5
		173±2	–	–	33.0±0.5	165.0±0.5
		195±2	–	–	42.0±0.5	210.0±0.5
		III stage				
		234±2	–	–	55.0±0.5	275.0±0.5
	After 15 days of storage at 2±2 °C	I stage				
		89±2	6.0±0.5	30.0±0.5	–	–
		II stage				
		115±2	–	–	25.0±0.5	100.0±0.5
		167±2	–	–	35.0±0.5	175.0±0.5
		198±2	–	–	45.0±0.5	225.0±0.5
		III stage				
		225±2	–	–	56.0±0.5	280.0±0.5
	After 4 months storage at −18±2 °C	I stage				
		86±2	8.0±0.5	40.0±0.5	–	–
		II stage				
		110±2	–	–	25.0±0.5	100.0±0.5
		164±2	–	–	40.0±0.5	200.0±0.5
		195±2	–	–	47.0±0.5	235.0±0.5

Continuation of table 3.14

1	2	3	4	5	6	7
		III stage				
		223±2	–	–	58.0±0.5	290.0±0.5
Developed TF sample with sesame seed concentrate	Freshly made	I stage				
		105±2	–	–	8.0±0.5	40.0±0.5
		II stage				
		177±2	–	–	24.0±0.5	120.0±0.5
		205±2	–	–	35.0±0.5	175.0±0.5
		III stage				
		245±2	–	–	48.0±0.5	240.0±0.5
	Freshly made (defrozen)	I stage				
		103±2	–	–	10.0±0.5	50.0±0.5
		II stage				
		170±2	–	–	24.0±0,5	120.0±0.5
		200±2	–	–	36.0±0.5	180.0±0.5
		III stage				
		243±2	–	–	50.0±0.5	250.0±0.5
	After 15 days of storage at 2±2 °C	I stage				
		98±2	3.0±0.5	15.0±0.5	–	–
		II stage				
		120±2	–	–	12.0±0.5	60.0±0.5
		175±2	–	–	24.0±0.5	120.0±0.5
		203±2	–	–	36.0±0.5	180.0±0.5
		III stage				
		240±2	–	–	48.0±0.5	240.0±0.5
	After 4 months storage at −18±2 °C	I stage				
		98±2	7.0±0.5	35.0±0,5	–	–
		II stage				
		115±2	–	–	19.0±0.5	95.0±0.5
		170±2	–	–	32.0±0.5	160.0±0.5
		200±2	–	–	44.0±0.5	220.0±0.5
		III stage				
		240±2	–	–	55.0±0.5	275.0±0.5

The first stage, which causes the beginning of moisture removal from the TF control for a freshly made sample and freshly made immediately after defrosting, occurs at a temperature of 100±2 °C, as after 15 days and as 4 months of storage. During the second stage of endo-effects in these TF samples removes the moisture

inherent in the bound moisture, as are the maximums of the same samples in the third stage, which causes the final destruction of the structure due to significant moisture loss. Thus, it was found that the highest loss of moisture was experienced by the TF samples after storage under both regimes, which is probably due to the ability of the starch to retain moisture, but retrogradation (aging) occurs. In this case, the moisture during storage is bound by pectin and other prescription components with hydrophilic properties (the action of starch is weakened). This causes a decrease of temperature influence for the destruction of certain chemical bonds between the TF prescription components during storage.

Summarizing the results of experimental studies to study the kinetic parameters of endothermic TF processes, the following conclusion can be drawn. Sesame seed concentrate contributes to the resistance of TF to high temperatures and reduces moisture mass loss. For both TF which stored under freezing, the peaks indicate a greater susceptibility to the removal of bound moisture in such samples. Moisture mass losses are more significant for TF samples (control) which were storaged at low temperature.

3.5.2.5 Determination the amount of frozen moisture

An important role during the TF storage is played the mass fraction of moisture in the filling, which characterizes the consistency, determines the physical, chemical and structural-mechanical properties throughout the shelf life [99; 131; 142; 178].

Moisture bonding forms, including the amount of free and bound moisture, were investigated using a low-temperature calorimetric method. Its essence is to record the heat released during the phase transition of water to ice [27; 175; 178; 239; 256]. As is known, only free moisture is involved in the phase transition. It is in the free state of intercellular space and easily freezes, unlike bound moisture. With its freezing, the concentration of salts in the intercellular solution increases, which causes the cryoscopic temperature to shift to a lower one. The freezing of moisture occurs gradually, until a continuous solid mass is reached, called eutectic [39; 163; 178; 266]. The change in the amount of free moisture in TH during storage under traditional conditions is shown in Fig. 3.9. It is not advisable to carry out such studies for filling which has already been exposed to low temperatures (freezing and storage at –18±2 °C).

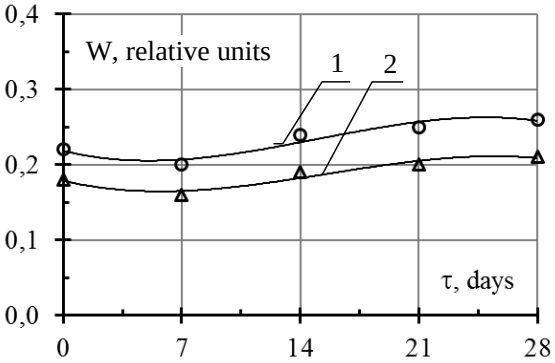


Figure 3.9. Dependence of the content of freezed (free) moisture TF on storage time: 1 - TF control sample; 2 - developed TF sample with sesame seeds concentrate

In Fig. 3.9 shows that the amount of frozen (free) moisture in the TF during the whole storage period increases. Such an increase of the free moisture content in the TF indicates damage to the structure and the weakening of interactions between the recipe components that are activated over time. It is revealed that during storage in TF with a plant additive less freezed moisture is released. Thus, it was found that the amount of frozen moisture depends on the formulation composition of TF: the presence in their recipe composition of the concentrate has a positive effect on the occurrence of intermolecular interactions between the ingredients, which is due to a decrease in frozen moisture.

Summarizing the above, the results of the study of the physicochemical properties of the proposed thermostable filling using dairy raw material and sesame seeds concentrate can be presented in two directions. The first area concerns the plant protein supplement and proves the feasibility of its use in TF technology. Thus, sesame seeds concentrate contributes to: increase of MHA, moisture retention, reduction of weight loss and amount of free moisture. The second direction - freezing - is manifested in a slight decrease of MHA and the destruction of the structure, a greater susceptibility to the removal of moisture.

3.6 Study of rheological properties of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

3.6.1 Determination of strength

One of the important indicators that determines the changes in the properties of TF throughout the shelf life is the strength indicator. In particular, the influence of low temperature on the texture properties of the product leads to certain negative changes: as a result of the destructive action of ice crystals, the structure of TF after defrosting is disturbed and loosened, and moisture is lost. With the help of the Valent device, the strength of the proposed TF samples was determined (Fig. 3.10).

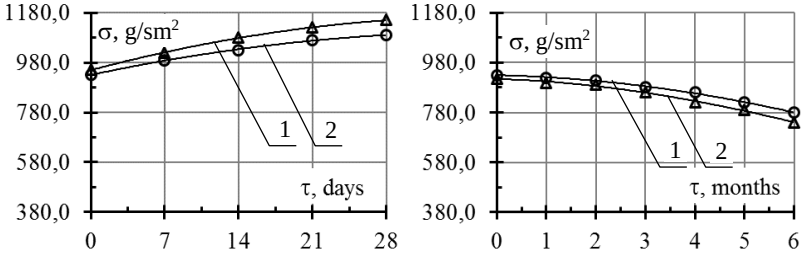


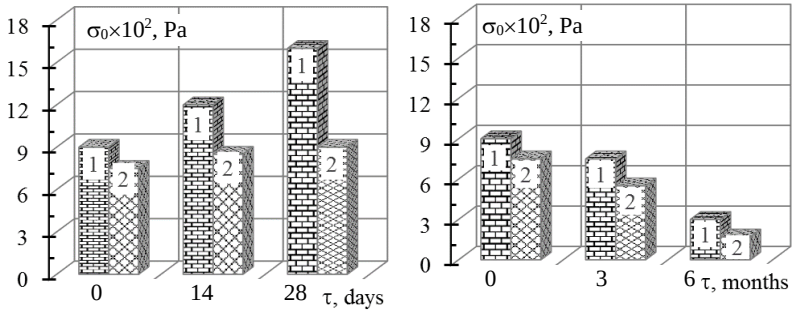
Fig. 3.10. Dependence of TF strength on the duration of storage at a temperature: a) 2±2 °C; b) –18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seeds concentrate

The results of the strength study show that TF samples with the addition of sesame seed concentrate at storage temperatures of 2±2 and –18±2 °C have slightly lower values of strength than similar samples without concentrate. Also in the course of data analysis Fig. 3.11 it was proved the strength of the test samples with a shelf life of 28 days at 2±2 °C was increased, and in the case of storage at –18±2 °C for 6 months, the indicators decreased. In case of TF samples storage at -18±2 °C for 6 months, there is a slight decrease in the strength indicator, mainly during the first 4 months: for the control and developed TF this indicator after 4 months is 862.5 and 855 g/cm^2, respectively, and after 6 months - 800 and 792.5 g/cm^2. The established change in the strength of TF indicates that the presence in the TF composition of sesame seeds concentrate helps to reduce the

strength of the filling and gives a more plastic consistency; this is confirmed by subsequent studies.

3.6.2 Determination of the shear stress

The studies were performed on a penetrometer, which allows to measure the amount of the product deformation during the stress on it. According to the obtained values, the limiting shear stress of TF under different storage regimes was determined by the calculation method (Fig. 3.11).



a) b)

Рис. 3.11. Dependence of the maximum shear stress of TF on the duration of storage at temperatures: a) 2±2 °C; b) –18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seeds concentrate

In Fig. 3.11 shows a decrease in the shear stress of the TF samples with the addition of a sesame seed concentrate, i.e. a decrease in their resistance. From the results of determining the shear stress, it can be stated that at low storage temperatures, the TF samples lose their resistance to deformation action; this indicates the destruction of the structure. TF with sesame seed concentrate has less resistance, which contributes to the formation of a softer structure. The trend identified is probably related to the structure, absorption and retention properties of moisture, the presence of a large number of hydrophilic and hydrophobic groups in the case of the combined use of dairy and plant components.

3.6.3 Study of structural and mechanical properties

Much of the rheological parameters of the proposed filling can be determined during mechanical loading. During loading, the TF samples are deformed and subjected to a certain stress, which is the integral beginning of the forces of internal interaction of the recipe

components with each other. According to A.P. Rebinder's classification, dispersed, colloidal and high molecular systems are divided into liquid and solid. In view of this, TF has the properties of a solid body. As you know, such bodies are characterized by certain indicators: elasticity, plasticity, strength and other characteristic properties, which are determined by the relative deformation of the product during the stress for a certain time. These changes in the structural and mechanical parameters of the TF during storage under different conditions are shown in Tables 3.15 and 3.16 and in the form of creep deformation curves of the prototypes (Figs. 3.12 and 3.13).

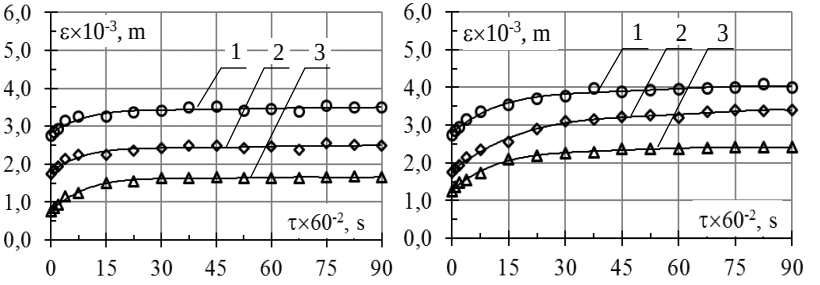


Fig. 3.12. Dependence of relative compression deformation of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature 2±2 °C on the time of stress: 1 – freshly made sample; 2 – sample after 14 days of storage; 3 – sample after 28 days of storage

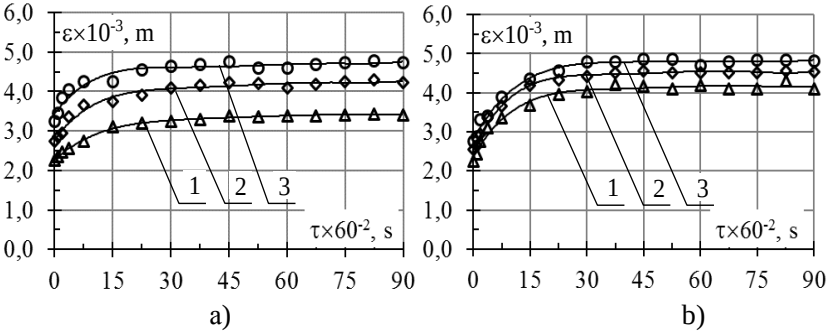


Fig. 3.13. Dependence of relative compression deformation of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature -18±2 °C on the time of stress: 1 – freshly made sample; 2 – sample after 3 months of storage; 3 – sample after 6 months of storage

Table 3.15 – Structural-mechanical characteristics of TF at storage temperature 2±2° C

Name of indicator	TF control sample			Developed TF sample with sesame seed concentrate		
	Duration of storage at temperature 2±2 °C, days					
	0	14	28	0	14	28
Reverse deformation ($\gamma_{rd.}$), m×10^3	3.37	2.24	1.66	3.84	3.20	2.32
Irreversible deformation ($\gamma_{ird.}$), m×10^3	0.04	0.18	0.11	0.18	0.18	0.18
Total deformation (γ_{td}), m×10^3	3.40	2.42	1.77	4.02	3.38	2.50
Shear stress (τ), Pa	1498.86	1498.86	1498.86	1498.86	1498.86	1498.86
Pliability (I), Pa^{-1}×10^6	2.27	1.61	1.18	2.68	2.25	1.67
Conditionally instantaneous modulus of flexability (G_f), Pa×10^{-5}	5.93	9.86	15.36	5.26	7.04	11.42
High elastic module (G_{el}), Pa×10^{-5}	17.84	20.93	21.91	15.17	14.03	14.92
Plastic viscosity (η^*_0), (Pa×s)×10^{-9}	225.00	45.00	74.90	45.00	45.00	45.00
The ratio of deformation inverse to total (K)	0.99	0.93	0.94	0.96	0.95	0.93
Viscosity of elastic aftereffect (η_{el}), (Pa×s)×10^{-7}	62.45	97.75	102.19	86.47	62.45	72.53
Relative flexability (Fl), %	74.27	62.91	55.20	70.92	63.03	52.56
Relative plasticity (Pl), %	1.06	7.45	6.11	4.48	5.33	7.21
Relative elasticity (El), %	24.68	29.64	38.69	24.60	31.54	40.22
Relaxation period (Θ), s×10^{-3}	505.20	67.08	83.00	115.08	95.88	69.48

Table 3.16 – Structural-mechanical characteristics of TF at storage temperature -18±2° C

Name of indicator	TF control sample			Developed TF sample with sesame seed concentrate		
	Duration of storage at temperature –18±2 °C, months					
	0	3	6	0	3	6
Reverse deformation ($\gamma_{rd.}$), m×10^3	3.26	4.14	4.54	4.20	4.48	4.66
Irreversible deformation ($\gamma_{ird.}$), m×10^3	0.11	0.07	0.07	0.18	0.18	0.11
Total deformation (γ_{td}), m×10^3	3.37	4.21	4.61	4.38	4.66	4.77
Shear stress (τ), Pa	1498.86	1498.86	1498.86	1498.86	1498.86	1498.86
Pliability (I), Pa^{-1}×10^6	2.25	2.81	3.07	2.92	3.11	3.18
Conditionally instantaneous modulus of flexability (G_f), Pa×10^{-5}	7.77	4.85	4.20	4.79	4.53	4.29
High elastic module (G_{el}), Pa×10^{-5}	11.25	14.30	15.48	14.09	12.88	12.79
Plastic viscosity (η^*_0), (Pa×s)×10^{-9}	74.90	112.00	112.00	45.00	45.00	74.90
The ratio of deformation inverse to total (K)	0.97	0.98	0.98	0.96	0.96	0.98
Viscosity of elastic aftereffect (η_{el}), (Pa×s)×10^{-7}	37.47	49.96	72.53	41.25	48.88	40.87
Relative flexability (Fl), %	57.24	73.38	77.43	71.57	71.13	73.15
Relative plasticity (Pl), %	3.21	1.71	1.56	4.11	3.87	2.27
Relative elasticity (El), %	39.55	24.90	21.01	24.31	25.00	24.58
Relaxation period (Θ), s×10^{-3}	163.00	310.20	340.20	125.88	134.28	233.00

In Fig. 3.12 it can be seen that during the storage of TF under the traditional conditions, the samples become less fluid, compacted, probably due to on the one hand, to the redistribution of moisture if the bonds are stabilized and, on the other due to syneresis. Instead, tthe fluidity for the corresponding samples (depending on the storage time) stored in the frozen state is increased (Fig. 3.13). This is due to the "loosening" of the structure by the negative influence of ice crystals. In general, it can be argued that freezing contributes to increased fluidity.

However, due to the analysis of changes in the structural and mechanical characteristics of the TF during deformation, the difference between them during storage at a temperature of -18±2 °C was established. Thus, during the comparison of the TF sample freshly made (it was frozen and immediately unfreez) and after 6 months of storage the increase of the deformation curves is revealed. This trend is true only for samples stored in a frozen state. Such a change is likely to be caused by the effect of low temperature on the change in the moisture state, which in turn affects the structure of the filling.

Summarizing the data on the change in the rheological properties of TF with different formulations and the influence of freezing, we can state the following. TF samples during storage at a traditional temperature acquire a strong and dense structure, probably due to the physico-chemical changes in the interactions between the recipe components. It was found that a TF sample with a plant protein supplement had a more uniform change in storage curves and a softer structure, as evidenced by the deformation curves. Opposite changes have low-temperature TF samples for 6 months. As is known, during storage in a frozen state, moisture enters a crystalline state, and crystals of different sizes are formed, resulting in the possibility of damage to the structure. Therefore, after defrosting the filling, there is a softening of its structure, the so-called "loosening".

3.7 Determination of the temperature influence on the technological properties of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

Of course, the thermal influence is a particular importance in the manufacture of thermostable filling. Temperature causes changes in heat exchange, physico-chemical, structural-mechanical and technological properties of the food system. Because of the temperature influence, strong chemical bonds can be broken. All of this leads to the rearrangement of the component molecules and the formation of new bonds. As you know, thermostable filling is characterized by a structure that does not change its physicochemical and, in particular, texture properties with a temperature action of about 200 °C for (10…15)×60 s [69; 70; 71; 93; 214; 215]. In the course of the experimental studies, in particular the establishment of moisture bound forms, the positive effect of sesame seed concentrate on a number of physicochemical properties of the filling was revealed. Thus, the concentrate promotes moisture retention and increases the moisture-holding ability of the product. Therefore, it is advisable to find out what effect the sesame seed concentrate has on the technological properties of the developed filling.

3.7.1 Change of thermal resistance

One of the main technological properties in the production of thermostable filling using dairy raw materials and sesame seeds concentrate is thermal stability, which means the temperature action that the product can withstand without changing its properties. To detect the thermostable properties, the duration of the action of temperature in the range of 100…220 °C for filling samples with different formulations, which were stored under different conditions was studied. The dependence of thermal stability on temperature ($\tau = f(t)$) has an inverse dependence. The thermal stability of the TF samples stored at 2±2 °C was determined immediately after manufacture, on the 14th and 28th day of storage (Fig. 3.14). However, the thermal stability of TF samples stored at –18±2 °C was investigated immediately after manufacture, on the 3rd and 6th month of storage (Fig. 3.15).

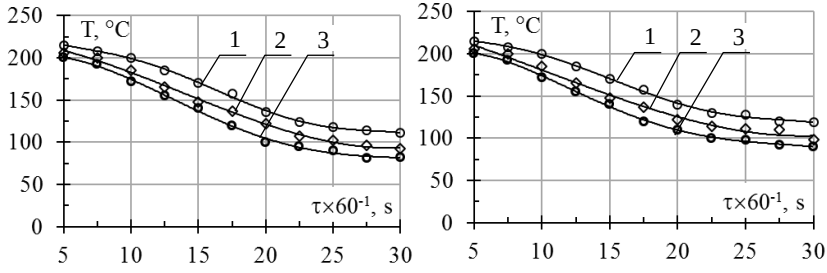


Fig. 3.14. The dependence of thermal stability a) TF control sample and b) the developed TF sample with sesame seeds concentrate at a storage temperature of 2±2 °C on the influence of high-temperature processing: 1 – freshly made sample; 2 – sample after 14 days of storage; 3 – sample after 28 days of storage

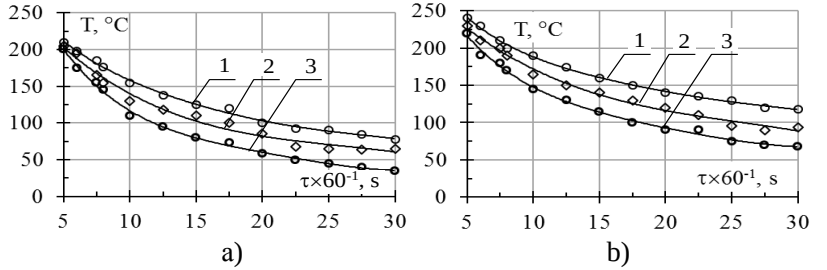


Fig. 3.15. The dependence of thermal stability a) TF control sample and b) the developed TF sample with sesame seeds concentrate at a storage temperature of –18±2 °C on the influence of high-temperature processing: 1 – freshly made sample; 2 – sample after 3 months of storage; 3 – sample after 6 months of storage

According to Fig. 3.14 and 3.15, there is an intense decrease in the thermal stability of all TF samples during storage under both conditions, indicating syneresis.

Freezing has been shown to reduce the thermal stability of the filling. Probably, as a result of the transition of free moisture to the crystalline state during storage of TF at –18 ± 2 °C, ice crystals of various sizes are formed, which cause damage to the structure of the filling. This explains the slight decrease in thermal stability, since

it reduces the connexion strength between the recipe components [16; 31; 67; 93 135; 220].

Comparing the data of Figures 3.14 and 3.15, the undeniable positive effect of sesame seed concentrate - a plant protein supplement increases the thermal stability of TF can be noted. This means that the developed filling, which contains in its recipe composition of sesame seeds concentrate, experiences less negative changes in its properties than the product without plant protein additives. This indicates the formation in the developed TF sample with sesame seed concentrate stronger interactions between the recipe components: high thermal stability is likely due to the action of intermolecular interaction forces, namely the increase of the interaction of surface layers and base phases [90; 233].

Therefore, it is established that the highest values of thermal stability have developed thermostable filling with sesame seeds concentrate. The results of the thermal stability study of the developed TF samples with concentrate after defrosting (freshly made, after storage for 3 and 6 months) are characterized by a similar trend of change of the indicator.

The above trend is also characteristic for filling control samples. Carrying out control samples of filling which stored under traditional conditions, then for a freshly made control sample of TF the thermal stability decreases from 28×60 to 11×60 s; for the sample examined for the 14th day, from 25×60 to 9×60 s; for the sample examined on the 28th day, from 20×60 to 7×60 s. Changes in the thermal stability of the control samples stored in the frozen state (fresh, after storage for 3 and 6 months) are as follows: from 28×60 to 11×60 s; from 15×60 to 7×60 s; from 10×60 to 3×60 s.

3.7.2 Change of melting temperature

Particular attention is paid in the production of thermostable fillings to the melting point, the temperature at which the product melts. It largely depends on the formulation components (together, the formulation components can both increase and decrease this temperature), in particular on their ability to form strong intermolecular interactions [93; 237 ; 274; 284; 288].

In Fig. 3.16 shows the change in the melting point of TF samples with different formulations, which were stored under different conditions.

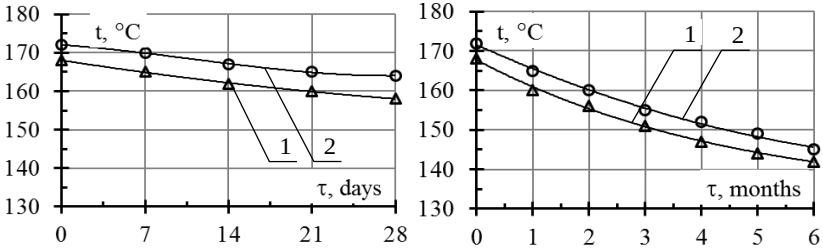


Fig. 3.16. Dependence of the TF melting point on the duration of storage at temperature: a) 2±2 °C; b) –18±2 °C; 1 – TF control sample; 2 – developed TF sample with sesame seeds concentrate

The above data (Fig. 3.16) show that during storage under different conditions for both TF (samples of TF with and without sesame seed concentrate), a decrease in melting point is observed. And freezing helps to reduce the melting point (there is a "loosening" of the structure due to the breakdown of bonds of different nature).

During the comparison of the melting point parameters of the studied samples, an increase in the melting point values in TF with a plant protein additive - a sesame seed concentrate, was recorded. This positive effect of sesame seeds concentrate on the melting point of the filling is due to the uniform distribution of moisture in the structure of the product, which during freezing causes slight damage to the structure [16; 31; 67; 135; 220].

After analyzing the results of both studies on changes in thermal stability and melting point, we can conclude. First, the long-term storage of the filling in two different conditions contributes to the reduction of thermal stability and melting point. This, as noted above, is mainly due to a decrease in moisture-holding ability and loss of moisture (syneresis). Secondly, the presence of sesame seed concentrate in the filling recipe composition has a positive effect on the technological properties of the product due to the formation of different forms of moisture bond: there is an increase in thermal resistance and melting point in products with the plant protein supplement. Thirdly, the freezing, due to the destruction of the skeleton filling with ice crystals, slightly reduces the technological characteristics of the product in accordance with the above trends.

3.8 Technology of functional beverages

The modern market is regularly replenished with new health products. The market of functional beverages is developing at a particularly fast pace, as for producers beverages are the most convenient object for the introduction of any ingredient, including functional, without fundamental changes in the technological process. Consumption of beverages containing nutrients is an effective means of strengthening the protective functions of the human body [21].

To ensure the real physiological activity of the drink and high organoleptic characteristics, food functional ingredients must meet the following requirements:

- useful properties of ingredients must be scientifically substantiated, physiological effects revealed for each;
- when introducing several functional ingredients, it is necessary to study their interaction and possible synergistic effects due to the complex effect on the body;
- ingredients must be safe and stable during storage;
- each ingredient must have accurate physico-chemical characteristics, which are reliably determined using special methods of analysis;
- the introduction of functional ingredients should not reduce the nutritional value of the product [21].

Vitamins, vitamin-like and mineral substances, water-soluble plant extracts that increase the body's adaptive capacity (flavonoids, terpenoids, anthocyanins, glycosides), as well as soluble dietary fiber are used for the production of functional drinks [23]. The specific effect of soluble dietary fiber on the human body is associated with several effects: feeling of satiety, ability to reduce dietary glycemia, prebiotic properties, microbial degradation of polysaccharides, accompanied by the formation and utilization of short-chain and volatile fatty acids, anti-carcinogenic effect, enterosorbent action. The norm of physiological need for soluble dietary fiber in adults is 2.0 g per day [18].

The most promising soluble dietary fibers include pectins, gum arabic, inulin and fructooligosaccharides.

Pectins provide the texture of the drink, forming solutions of different viscosities and gels in water, their specific physiological

action is associated with the ability to lower blood cholesterol, normalize the activity of the gastrointestinal tract, remove some toxins and heavy metals from the body. As acidic polysaccharides, they show a synergistic effect with protein molecules, which provides stabilization of the latter in acidic beverages [24, 25].

Pectin-containing nectars. Specialists of the National University of Food Technologies have developed drinks with a high content of pectin "Pectin-containing nectars" (TS U 199-020709038-001: 2005). It is known that in hydrated form pectins show their functional and pharmacological properties in full.

The composition of pectin-containing nectars includes vegetable puree of carrots, pumpkin, fruit puree of apples, apricots, peaches, currants, cherries, pectin concentrate or pectin, sugar, citric acid, infusions of plant raw materials (lemon balm, mint), which provide excellent taste properties, high nutritional and biological value. The product is rich in dietary fiber, easily digestible carbohydrates, organic acids, vitamins, micro-microelements.

It should be noted that pectin in combination with biologically active substances of vegetables, fruits and berries enhances their biological functions.

It should be noted the composition and biologically active value of the main components of pectin-containing nectars: puree of pumpkin, Pumpkin puree contains polysaccharides (fiber, pectin), monosaccharides and disaccharides (glucose, fructose, sucrose), organic acids (mainly apple). Vitamin composition is represented by vitamins C, B_1, B_2, carotene. Especially valuable for the child's body vitamin D, which enhances the viability and accelerates the growth of children. Other compounds useful for the body are used to improve the functional activity of the intestines, kidneys, liver. Pumpkin puree is a real storehouse of minerals, it contains calcium, potassium, phosphorus, iron, copper, fluorine, zinc, which have a positive effect on hematopoiesis. Pumpkin pulp is used to prevent anemia and atherosclerosis, is a good regulator of digestion and due to the high content of pectin helps to eliminate cholesterol.

Pumpkin drinks are recommended to include in the diet of patients with hepatitis and cholecystitis, people with gallstones, chronic colitis and enterocolitis, diseases of the cardiovascular

system (hypertension, atherosclerosis with circulatory failure), acute nephritis and pyelonephritis.

Carrot puree - finely grated, homogenized carrot pulp, is a source of carbohydrates, biologically active substances and minerals. Carbohydrates are mainly fiber, pectin, hemicellulose, sucrose, glucose and fructose; nitrogenous substances - amino acids and easily soluble proteins that are well assimilated by humans. Carrot puree is rich in vitamins, in particular, carotene, which in the liver and small intestine in the presence of fat is converted into vitamin A. This vitamin increases the body's resistance to infectious diseases, its insufficient content leads to decreased visual acuity and can cause complete vision loss. Therefore, it is recommended for people whose profession is associated with eyestrain. Carrot puree contains phospholipids, lecithin and styrene. Inositol, which is found in the pulp, mainly acts as a prophylactic and therapeutic agent for atherosclerosis, because it has the ability to improve lipid metabolism in the body. Among the minerals can be distinguished potassium, phosphorus, chlorine and magnesium. In terms of magnesium, carrot raw materials outperform all other vegetable raw materials. It affects the dilation of blood vessels, activates intestinal motility. Carrot puree has numerous trace elements - aluminum, boron, vanadium, iron, iodine, cobalt, copper, manganese, zinc. Therefore, carrot drinks are recommended for patients with reduced thyroid function. Biologically active substances (pectin, vitamins, phenolic compounds, minerals), which are part of fruit and berry purees (apples, apricots, peaches, currants), provide high biological value, which contributes to:

– strengthening the immune system, blood vessels, heart and circulatory system;
– recovery of the digestive system;
– binding of free radicals;
– strengthening the nervous system;
– activation of cellular metabolism and hematopoietic processes;
– lowering blood pressure, blood cholesterol levels;
– strengthening the protective function of cell membranes of the body.

Nectars are made from environmentally friendly raw materials, do not contain synthetic dyes and preservatives.

Table 3.1 - Organoleptic characteristics of pectin-containing nectars

Indicators	Characteristic
Appearance and consistency	Homogeneous, opaque liquid with fine pulp. Slight stratification of the mass is allowed
Taste and smell	Inherent in the raw material from which the nectar is made. Not allowed foreign taste and smell
Color	Inherent in the raw material

Table 3.2 - Physico-chemical parameters of pectin-containing nectars

Indicators	Values
Mass fraction of dissolved solids,%, not less	9.5
Mass fraction of pectin,%, not less	0.5
pH, not more	4.2
Mass fraction of mineral impurities,%, not more	0.02
Mass fraction of impurities of plant origin	not allowed

Pectin-containing nectars are highly valued and recommended by the Ministry of Health of Ukraine as an additional source of pectin in the diets of various age and occupational groups, including those living or working in adverse environmental or industrial conditions.

Pectin-containing beverages "Sunski rosy" (TS U 18. 459-98) are made from fresh vegetables, fruits, berries by blending pectin extract from pomace with juices or puree, which allows you to get drinks with pulp and without pulp. Honey, fructose, glucose-fructose or high-fructose syrups can be used as sweeteners in beverages. This makes it possible to drink drinks to persons with metabolic disorders, for example, patients with diabetes mellitus [26].

Organoleptic and physicochemical parameters of "Sunski rosy" drinks are presented in tables 3.3 and 3.4.

The technological process of beverage production is as follows. In a mixer equipped with a stirrer, load according to the recipe all the components of the drink, mix until a homogeneous mass, homogenize. Beverages are packaged at a temperature of 90 ± 2 ° C on automatic fillers in glass jars with a capacity of not more than 0.25 liters, or at a temperature of 70 ± 2 ° C in glass jars with a

capacity of up to 3 liters. The jars are then rolled up, sterilized and cooled. The finished product is stored in warehouses at a temperature of 0… 20 ° C and relative humidity of not more than 75%.

Table 3.3 – Organoleptic characteristics of "Sunski rosy" drinks

Indicators	Characteristic
Appearance and consistency	Homogeneous liquid with evenly distributed finely divided mass. Slight delamination and small sediment at the bottom of the cans is allowed
Taste and smell	Pleasant, inherent in vegetables, fruits, berries or mixtures thereof, from which the drink is made. Foreign taste and smell are not allowed
Color	Homogeneous, corresponding to the color of vegetables, fruits, berries or mixtures thereof, from which the drink is made

Table 3.4 – Physicochemical parameters of "Sunski rosy" drinks

Indicators	Values
Mass fraction of dissolved solids,%, not less	11.0
Mass fraction of pectin,%, not less	0.5
Mass fraction of titrated acids (in terms of malic acid),%, not more	0.5
Active acidity, pH	3.0…3.3
Mass fraction of mineral impurities	not allowed
Mass fraction of impurities of plant origin	not allowed

The biologically active additive, phytopectin drink "Suziria Leva" (TS U 02070938.014-2000) is made on the basis of apple pectin extract and alcoholic apple juice with the addition of infusions and decoctions of medicinal plants: oregano, St. John's wort, linden, lemon balm, mint, chamomile, dog-rose [27, 28].

Table 3.5 – Organoleptic characteristics of phytopectin drink "Suziria Leva"

Indicators	Product features
Appearance	Not a clear liquid, a slight precipitate is allowed. No extraneous inclusions.
Taste	Sweet and sour, soft, harmonious, with a grassy tone. The bouquet has an apple flavor.
Smell	Characteristically pronounced apple smell with a bouquet of herbs.
Color	From pink-brown to brown.

Table 3.6 – Physicochemical parameters of phytopectin drink "Suziria Leva"

Indicators	Values
Mass fraction of sugar, g/100cm^3	14.0±0.5
Alcohol, %	12.0±0.5
Mass fraction of extractives, g/100cm^3	16.0±0.6
Mass fraction of pectin substances, g/100cm^3, not less	0.5
Mass fraction of titrated acids (in terms of citric acid), g/100cm^3	0.5±0.2
The content of bioflavonoids, μg/ml, not more	10.0

The Institute of Ecological Hygiene and Toxicology L. Medved conducted clinical studies and concluded the clinical aspects of the use of the drink, according to which the product has a pronounced biological effect.

3.9 Technology of canning products

In the canning industry, pectin is used in the production of jelly products: jellies, confiture, jam, as well as health products (purees, kissel, juices, beverages, canned vegetables, etc.), as well as sauces and ketchups [29].

In addition to pectin, jelly canned goods include fruits and berries (apricots, plums, cherries, strawberries, tangerines, apples, etc.), sugar, acids (citric, tartaric, malic), dyes and flavors.

To obtain products with a jelly structure, important technological factors that affect the gelation and structural and mechanical properties of products are: type of pectin and its dosage, type of fruit, dry matter content in the product, calcium content in fruits and water, pH, temperature and duration packing.

Pectin-containing puree "Darunok" (TS U 18.458-98) and ***pectin-containing desserts "Barvy Ukrainy"*** (TS U 18019595-32-97) are made using hydrohydrated and rubbed pomace - waste of juice production: apple, currant, rowan, carrot with a high content pectin, which are then blended with fruit or vegetable puree.

Organoleptic and physicochemical characteristics are presented in table. 3.7 and table 3.8.

Table 3.7 – Organoleptic characteristics of pectin-containing dessert "Barvy Ukrainy" and puree " Darunok "

Indicators	Product features	
	Dessert "Barvy Ukrainy"	**Puree " Darunok "**
Appearance and consistency	Homogeneous rubbed mass without seeds, skin particles and coarse core particles	Homogeneous rubbed mass without seeds, skin particles and coarse core particles
Taste and smell	Inherent in vegetables, fruits or berries from which the dessert is made	Inherent in vegetables, fruits, berries or mixtures thereof, from which the puree is made. Foreign taste and smell are not allowed
Color	Homogeneous, corresponding to the color of vegetables, fruits or berries from which the dessert is made	Homogeneous, corresponding to the color of vegetables, fruits, berries or mixtures thereof, from which the puree is made

The use of sweeteners such as fructose, glucose-fructose or high-fructose syrups gives the products dietary properties.

Both dry pectin and liquid pectin concentrate can be used to make pectin-containing desserts. On pectin concentrate the technology of production of fruit dessert which has pleasant taste and aroma, beautiful color, jelly consistence is developed. The production of dessert is carried out as follows. The pectin concentrate is decanted from the precipitate and filtered through a stainless steel sieve or through a cloth. The dessert should be completely transparent, without the inclusion of particles of fruit tissue. If the concentrate has a low dry matter content (12… 14%), it is boiled in a vacuum apparatus at a residual pressure of 8… 10 kPa.

Table 3.8 – Physicochemical parameters of pectin-containing dessert "Barvy Ukrainy" and puree " Darunok "

Indicators	Values	
	Dessert "Barvy Ukrainy"	Puree " Darunok "
Mass fraction of solids,%, not less	45.0	15.0
Mass fraction of pectin substances,%, not less	2.0	0.7
Mass fraction of titrated acids (in terms of malic acid),%	0.5…1.0	0.5
Active acidity, pH, not less	3.0	3.4
Mass fraction of mineral impurities,%, not more	0.03	0.02
Mass fraction of impurities of plant origin,%, not more	0.02	0.02

The boiling point is 45…50 ° C, which preserves the pectin, which is destroyed at higher temperatures. To the concentrate, boiled to 17… 18% of dry matter, is added hot filtered sugar syrup with a concentration of 70…73%. The mixture of concentrate and syrup is boiled in a vacuum apparatus at a residual pressure of 8…10 kPa to a concentration of 66% dry matter. When boiling is complete, the

product is sterilized at a temperature of 100 ° C. To the cooled jelly in the mixture add citric acid in the form of a 50% solution. Add acid to the product immediately before packing the dessert in jars. Recipes for pectin-containing fruit desserts are given in table 3.9.

Table 3.9 – Fruit and berry dessert recipe

Name of raw materials	Raw material consumption kg/tube	
	apple	cherry
Pectin concentrate	384	414
Natural cherry juice	-	184
Natural apple juice	206	
Sugar	322	355
Citric acid	1.2	1.0

Pectin-containing candied fruits. Candied fruits are fruits, berries, vegetables or their particles cooked in sugar or sugar molasses syrup, with the addition of certain types of food acids, dried, sprinkled with granulated sugar or glazed. The consumer properties of candied fruits are due to their pleasant taste, good assimilation, stability during storage, versatility of use both for direct consumption and for the manufacture of most confectionery products. The basis of candied fruits are carbohydrates, as well as organic acids and minerals.

The technology of pectin-containing candied fruits is based on the process of converting protopectin into a soluble form. The raw material is cut into pieces measuring 8...20 cm, blanched with hot steam for 8...15 minutes, kept in a solution of citric acid (pH= 2.5...3.0) at a temperature of 25...65 ° C for 1...3 hours for hydrolysis of protopectin, drain the pieces, and then spend two or three infusions of them in sugar syrup until complete saturation of candied fruits by sugar. After that, the candied fruits are separated from the syrup, dried and sprinkled with sugar [31].

The range of candied fruits is formed by various fruits and berries, as well as the use of zucchini, carrots, beets, pumpkins, peels of watermelons and melons. Candied fruits have a high content of soluble pectin (1.2…1.5%), transparent due to the formed pectin gel in the polysaccharide matrix of plant tissue. The taste of candied fruit is sweet or sour-sweet, typical of the type of raw material. Color is

close to the natural color of fruits or vegetables from which they are made. The consistency of the products is dense, gel-like, without lumps of crystallized sugar, the fruits are evenly cooked, easily cut. The mass fraction of dry matter in fruits and berries is not less than 83%, and in the peel of watermelons, melons, pumpkins, carrots, beets, zucchini - 80% . The total sugar content per invert, respectively, 75% and 72%.

Vegetable pectin-containing products: ketchup "Pektodar", sauces "Darunok poliv" and "Katran" (TU 18019595-29-95) [30].

The basis of "Pectodar" ketchup and "Darunok Poliv" sauce are tomato products, "Katran" sauce - horseradish. Pectin, extracts of beet and carrot , sugar, salt and spices are included in the "Pectodar" ketchup recipe.

Table 3.10 – Organoleptic characteristics of vegetable pectin-containing products

Indicators	Characteristics of pectin-containing products		
	Ketchup "Pektodar"	**Sauce "Darunok poliv"**	**Sauce "Katran"**
Appearance and consistency	Homogeneous rubbed mass without seeds, skin particles and coarse core particles. The presence of small particles of spices, particles of greens is allowed	Homogeneous rubbed mass without seeds, skin particles and coarse core particles. The presence of small particles of spices, particles of greens is allowed	Thick liquid. The presence of small particles of horseradish is allowed.
Taste and smell	Spicy, sweet and sour with a characteristic aroma of tomato products, vegetables and spices	Spicy, sweet and sour with a characteristic aroma of vegetables and spices	Spicy, characteristic of horseradish
Color	From light red to dark burgundy	From light red to dark burgundy	From pink to dark burgundy

Table 3.11 – Physicochemical parameters of vegetable pectin-containing products

Indicators	Ketchup "Pektodar"	Sauce "Darunok poliv"	Sauce "Katran"
Mass fraction of pectin substances,% not less	0.5	0.5	0.5
Mass fraction of solids,% not less	15.0	15.0	15.0
Mass fraction of chlorides,%	1.5…2.5	1.5…2.5	1.5…2.5
Acidity is titrated (in terms of malic acid), %, not more	1.1…1.5	1.1…1.5	1.1…1.5
Active acidity, pH, no more	2.5…3.5	2.5…3.5	2.5…3.5

"Darunok poliv" sauce is made using hydrolyzed puree of table beets and carrots, sugar, salt, pectin, spices; "Katran" sauce is icluded pectin, beetroot extract, sugar, salt, spices.

3.10 Confectionery technology

Due to the optimal application possibilities and numerous advantages, pectins are becoming increasingly important in the confectionery industry as texture-forming and gel-forming ingredients. The group of confectionery products covers a large number of different products that differ from each other in their textural properties. Pectins are used in the manufacture of jelly products, which include jelly and fruit marmalade, marshmallows, pastilles. Pectins are widely used in the manufacture of products such as cookies with layers, oriental sweets, jelly fillings for cookies, chocolate and caramel candies, marshmallows [32].

The main technological advantages of pectins in comparison with other hydrocolloids are their high ability to forming a gel, good solubility and temperature resistance at low pH values. Jelly products obtained with the help of pectins have a unique texture, which is created individually for each product, and characterizes its specific properties. The texture varies from strong and elastic to soft and viscous. Due to this texture and neutral taste, the products have a good natural taste of fruit raw materials or added flavors [33].

Apple pectin concentrate is a gelling agent for confectionery jelly products. In order to develop jelly products, in particular, marmalade, theoretical and experimental studies were conducted using apple pectin concentrate (APC) as a gelling agent. The technology of production of apple pectin concentrate was developed at the National University of Food Technology [34, 35]. The technology is introduced at the enterprises on processing of fruit and berry and vegetable raw materials and is made according to the developed normative and technical documentation (TS 15.8-19492247.014.2003 "Apple pectin concentrate"). Physico-chemical parameters of apple pectin concentrate are given in table 3.12.

Table 3.12 – Physico-chemical parameters of apple pectin concentrate

Indicators	Значення
Mass fraction of solids, %	6.4±0.2%
Mass fraction of pectin substances, %	3.0±0.2%
Active acidity, pH	3.0±0.2

Given the fact that in the production of marmalade products, pectin is used as a gelling agent, the ability of pectin concentrate to gel formation and the effect of sugar and acid on the strength of jellies were studied. The results of the study are presented in Fig. 3.2.

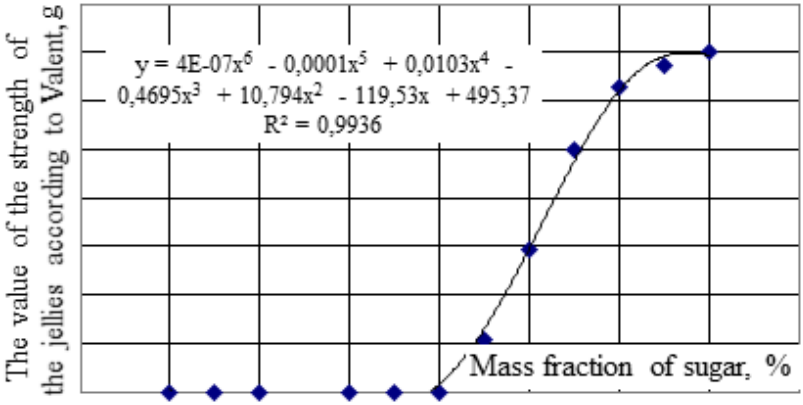


Figure 3.2 - Dependence of the strength of jellies on the concentration of sugar in pectin-sugar syrup

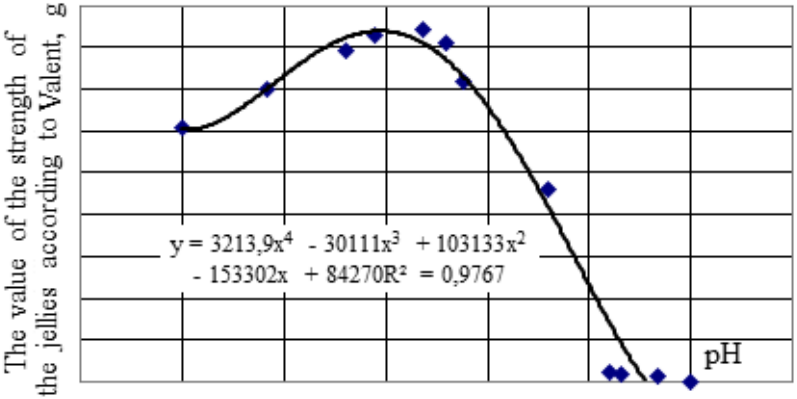


Figure 3.3 - The dependence of the strength of the jellies on the change in pH of the jelly mass

According to traditional technology, the formulation of pectin-based jelly marmalade includes the following recipe components: pectin, sugar, starch molasses, citric acid, sodium lactate, flavoring and coloring additives.

Based on the obtained data, the technology and recipe of jelly marmalade made with the addition of apple pectin concentrate were developed (table 3.13).

Table 3.13 – Recipe for jelly marmalade based on APC

Name of raw materials	Mass fraction of solids, %	Raw material consumption per 1000 kg of finished product	
		in reality, kg	in solids, kg
Pectin concentrate	6.40	900.0	58.0
White sugar	99.85	520.0	519.0
Molasses starch	78.00	170.0	133.0
Food essence	0.00	0.6	0.00
Food dye	0.00	0.1	0.00
Citric acid	98.00	1.0	0.10
Sodium lactate 40% solution	40.00	50.0	20.0
Weight of the finished product		1000.0	817.0

Marmalade. The development of jelly marmalade technology, made by using apple pectin concentrate, is based on the obtained research data [36].

The preparation of raw materials is carried out similarly to the classical technology: white sugar is sifted, citric acid solution and pectin concentrate are filtered.

Half of the sugar in the recipe is added to the pectin concentrate.

The mass is boiled to a solids content of 55 ... 60%. Then the second half of sugar is entered and boiling to solids content of 68 ... 70%. The temperature of the mass after boiling is approximately 107 ... 108º C, then it is cooled to a temperature of 70 .... 75º C, molasses, sodium lactate, flavoring and coloring substances, as well as a solution of citric acid are added. All components are thoroughly mixed. The finished marmalade mass is poured into molds. The duration of gelation is 15 ... 20 minutes. Marmalade particles are removed from the molds and dried at a temperature of 30 ... 35º C for 1 ... 2 hours at a humidity of 20 ... 30%. A crust is formed on the surface of the marmalade, which increases the adhesive forces, which promotes better sticking of sugar when sprinkled. After that, the marmalade is sprinkled with sugar and sent to drying, which takes place at a temperature of 40 ... 45º C for 20 ... 22 hours at a humidity of 20 ... 30%. The finished marmalade is packed in boxes and sent for sale.

The technological scheme of production of jelly mold marmalade using apple pectin concentrate is presented in Fig. 3.4.

Based on the analysis of the technology of jelly marmalade using apple pectin concentrate and traditional technology, we can conclude that the new technology can significantly reduce the duration of the production process. The main time savings are due to the exclusion from the technological process of the stage of preparation of pectin solution.

It is obvious that the use of this apple pectin concentrate can be cost-effective not only by reducing the cost of raw materials, but also by reducing the duration of the technological process of jelly marmalade production .

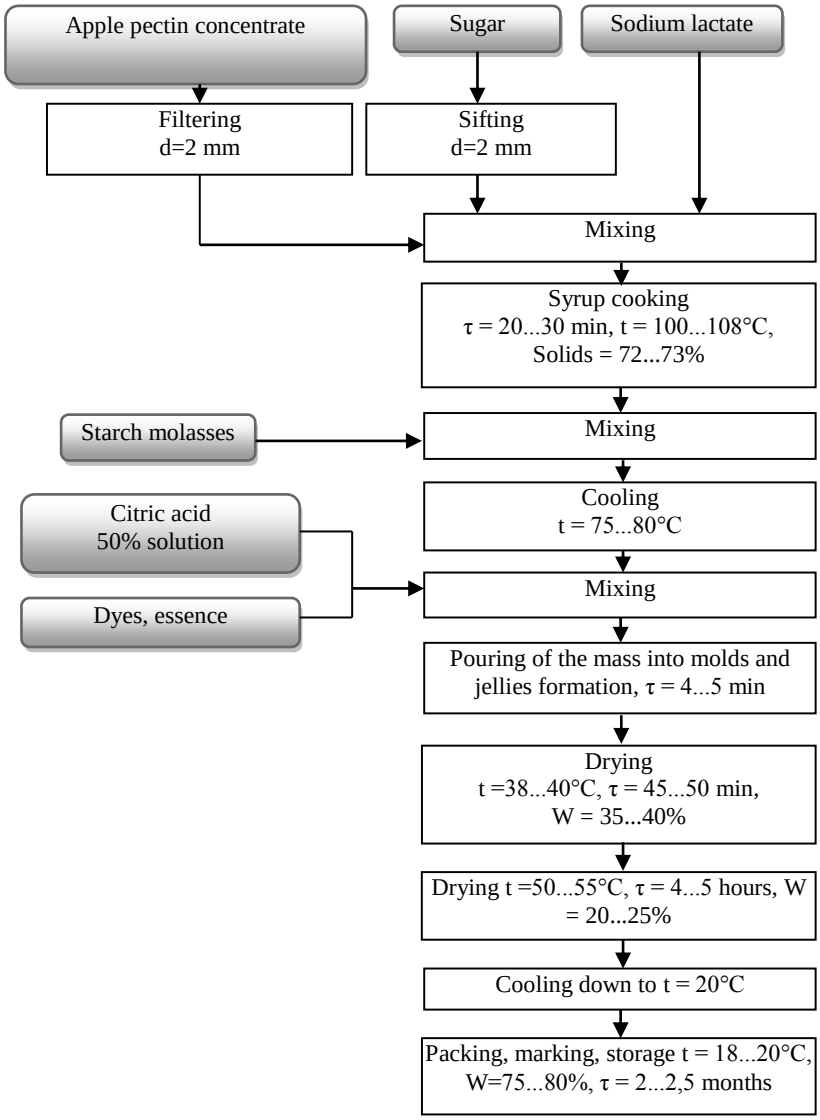


Figure 3.4 - Technological scheme for the production of jelly mold marmalade using APC

Research of structural and mechanical properties. Based on the obtained samples, the analysis and comparison of structural and

mechanical properties of the marmalade based on APC and traditional marmalade based on dry apple pectin were performed. The research was carried out on the scales of Kargin-Sokolova, the results are presented in Fig. 3.5.

Based on the obtained dependences, the main necessary rheological characteristics are calculated and their analysis and comparison are performed.

Determination of springiness. The springiness of the obtained samples is calculated by the formula:

$$Sp = \frac{\varepsilon_0}{\varepsilon_m} \cdot 100 \qquad (3.1)$$

where ε_o – springy conditional-instantaneous deformation, which occurs instantly under the action of the applied stress and disappears instantly after its removal;

ε_m – the maximum achieved deformation under the action of the applied stress.

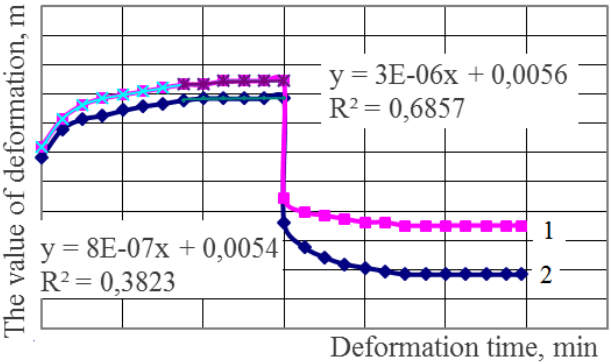


Figure 3.5 – Rheological characteristics of marmalade jellies: 1 – traditional marmalade; 2 – marmalade based on APC

$$\varepsilon_m^{APC} = 0{,}0054(mm)\ \ \varepsilon_m^{trad.} = 0{,}0057(mm)$$
$$\varepsilon_0^{APC} = 0{,}0044\,(mm)\ \ \varepsilon_0^{trad.} = 0{,}0046\,(mm)$$

$$Sp^{APC} = \frac{\varepsilon_0^{APC}}{\varepsilon_m^{APC}} \cdot 100 = \frac{0{,}0044}{0{,}0054} \cdot 100 = 81{,}48 \pm 0{,}4\,,$$

$$Sp^{trad.} = \frac{\varepsilon_0^{trad.}}{\varepsilon_m^{trad.}} \cdot 100 = \frac{0,0046}{0,0057} \cdot 100 = 80,70 \pm 0,4$$

It is shown that the value of springiness for marmalade based on APC is slightly higher than for traditional marmalade.

The modulus of instantaneous springiness is calculated by formula 3.2:

$$E_s = \frac{P}{\varepsilon_o} \tag{3.2}$$

To do this, it is necessary to determine the stress on the sample, which was calculated by formula 5.3.

$$P = \frac{F}{S} = \frac{F}{\pi r^2} = \frac{0,075}{3,14 \cdot 0,004^2} = 1492,8(Pa) \tag{3.3}$$

Therefore

$$E_s^{APC} = \frac{P}{\varepsilon_0^{APC}} = \frac{1492,8}{0,0044} = 339,3(\text{kPa / m}),$$

$$E_s^{\text{trad.}} = \frac{P}{\varepsilon_0^{trad}} = \frac{1492,8}{0,0046} = 324,5(\text{kPa / m}).$$

Determination of elasticity. Elasticity is calculated by the formula:

$$E = \frac{\varepsilon_{nd}}{\varepsilon_{sd}} \cdot 100 \tag{3.4}$$

where ε_{sd} – specific elastic deformation - completely reversible relative deformation: $\varepsilon_{sd} = \varepsilon_0 + \varepsilon_{ве}$;

ε_{hd} – highly elastic deformation - a relative deformation that gradually disappears after stress relief: $\varepsilon_{hd} = \varepsilon_{sd} - \varepsilon_0$;

$$\varepsilon_0^{APC} = 0,0044(mm) \qquad \varepsilon_0^{trad.} = 0,0046(mm)$$

ε_{sd} is equal to the coefficient b (the point of intersection of the tangent to the line of deformation and the axis "y") in the equation tangent to the deformation curve.

$$\varepsilon_{sd}^{APC} = 0,0051(mm) \qquad \varepsilon_{sd}^{trad} = 0,0055(mm)$$

Therefore

$$\varepsilon_{nd}^{APC} = 0{,}0051 - 0{,}0044 = 0{,}0007(mm)$$
$$\varepsilon_{sd}^{\text{trad}} = 0{,}0055 - 0{,}0046 = 0{,}0009(mm)$$

The elasticity of marmalade samples was calculated on the basis of data on specific elastic deformation and highly elastic deformation.

$$E^{APC} = \frac{\varepsilon_{nd}^{APC}}{\varepsilon_{sd}^{APC}} \cdot 100 = \frac{0{,}0007}{0{,}0051} \cdot 100 = 13{,}72 \pm 0{,}4,$$
$$E^{trad} = \frac{\varepsilon_{nd}^{trad}}{\varepsilon_{sd}^{trad.}} \cdot 100 = \frac{0{,}0009}{0{,}0055} \cdot 100 = 16{,}36 \pm 0{,}4$$

The modulus of elasticity is calculated by the formula:

$$E_e = \frac{P}{\varepsilon_{nd}}, \qquad (3.5)$$

$$E_e^{APC} = \frac{P}{\varepsilon_{nd}^{APC}} = \frac{1492{,}8}{0{,}0007} = 2{,}13(MPa/m),$$
$$E_e^{\text{trad}} = \frac{P}{\varepsilon_{nd}^{\text{trad}}} = \frac{1492{,}8}{0{,}0009} = 1{,}66(MPa/m).$$

Thus, the relative elasticity and modulus of elasticity of marmalade made on the basis of APC and marmalade made by traditional technology are almost the same.

Determination of plasticity. The relative plasticity was calculated by the formula:

$$Pl = \frac{\varepsilon_{pl}}{\varepsilon_m} \cdot 100 \qquad (3.6)$$

where ε_m – the maximum achieved deformation under the action of the applied stress;

ε_{red}, ε_{pl} – residual (plastic) deformation that does not disappear after removal of the applied stress for an infinitely long time: $\varepsilon_{red} = \varepsilon_{pl}$.

$$\varepsilon_{pl}^{APC} = 0{,}0024(mm) \qquad \varepsilon_{pl}^{trad.} = 0{,}0033(mm),$$

$$\varepsilon_m^{APC} = 0{,}0054(mm) \qquad \varepsilon_m^{trad} = 0{,}0057(mm),$$

$$Pl^{APC} = \frac{\varepsilon_{pl}^{APC}}{\varepsilon_m^{APC}} \cdot 100 = \frac{0{,}0024}{0{,}0054} \cdot 100 = 44{,}44 \pm 0{,}4,$$

$$Pl^{trad} = \frac{\varepsilon_{pl}^{trad}}{\varepsilon_m^{trad}} \cdot 100 = \frac{0{,}0033}{0{,}0057} \cdot 100 = 57{,}9 \pm 0{,}4 \cdot$$

Based on the obtained calculations, it was concluded that the relative plasticity of traditional marmalade is slightly higher than that of developed marmalade based on APC. However, the quality of the new marmalade is not reduced.

Data on the structural and mechanical properties of the investigated marmalade are presented in table. 3.14.

Table 3.14 - Structural and mechanical characteristics of marmalade jellies

Product	Springiness, %	Plasticity, %	Elasticity,%
Marmalade based on APC	81.48±0.4	44.44±0.4	13.72±0.4
Traditional marmalade	80.70±0.4	57.9±0.4	16.36±0.4

On the basis of the conducted researches the recipe and technology of production of new jelly marmalade on the basis of apple pectin concentrate is developed. An organoleptic evaluation of the obtained samples and existing ones on the market was performed. It is determined that in terms of organoleptic parameters the obtained samples are not inferior to the samples of marmalade made on pectin and present on the market of Ukraine.

The technology of marmalade “Apelsynovi ta lymonni chastky” ("Orange and lemon particles") based on apple pectin extract was developed [37].

Marmalade "Figured in chocolate". Marmalade technology based on low-esterified pectin, which was not used in the confectionery industry, has been developed. The proposed method of obtaining marmalade includes mixing dissolved in water low-

esterified pectin, sugar and molasses, boiling the mass to a solids content of 73… 74%, cooling to 60… 65 ° C, adding citric acid, sodium lactate, essences and dyes, mixing and pouring of the mass into molds, keeping for 1,0… 1,5 hours for jellies formation, extraction, drying to a solids content of 79%, glazing with chocolate glaze, cooling and packaging [38].

Jelly antimutagenic product. Jelly antimutagenic product contains natural juice of medicinal plants fruits, apple pectin concentrate, sugar, sodium lactate in the following ratio of ingredients:

natural juice of medicinal plants fruit	40 – 60%,
apple pectin concentrate	25 – 40%,
sugar	40 – 55%,
sodium lactate	0,3 – 0,5%.

The product is made of natural juice fruit with the pulp of viburnum, actinidia, henomeles, sea buckthorn, lemongrass, turf, elderberry. Natural juices of these plants contain a powerful complex of biologically active substances (vitamins: C, groups B, E, PP, etc .; carotene, higher fatty acids, phytosterols, pectins, flavonoids, macro- and micronutrients, etc.), which give the product a high biological values [41].

Apple pectin concentrate is used as a biologically active additive and as a gelling agent - gives the product a jelly texture. As a biologically active additive, apple pectin concentrate contains: pectin, phenolic compounds, organic acids, monosaccharides, etc., which give it the ability to bind heavy metals and radionuclides, remove toxins from the body, reduce cholesterol and blood sugar, to total recovery of the gastrointestinal tract.

The natural juice with the pulp of the medicinal plants fruits is mixed with apple pectin concentrate and sugar, boiled for 3… 5 minutes, added sodium lactate, served to forming.

The use of natural juices with the pulp of medicinal plants fruits and apple pectin concentrate makes it possible to produce jelly products with antimutagenic or gene-protective properties, with high biological value due to the presence of pectin, anthocyanins, phenolic and other biologically active substances [39, 40, 42].

Marshmallow products. Marshmallow products are obtained by whipping boiled fruit and berry puree with sugar and egg protein

and mixing with gelling agents. They have a foam structure reinforced with gelling agents. Foams are a dispersed system consisting of cells filled mainly with air and separated from each other by thin membrane of the dispersion medium. In marshmallow products, the dispersed phase is air, and the dispersion medium is a sugar-fruit-protein sol, which can turn into a gel. Appropriate viscosity of the initial solution and low surface tension at the liquid-air phase separation are required for the formation of foam. To facilitate the process of whipping and obtaining more stable foams as surfactants use egg protein. The low surface tension of the egg protein allows to reduce the thickness of the layer of medium between the bubbles with the formation of a large separation surface. At the same time, the viscosity prevents a decrease in the thickness of the layer, which can lead to its rupture and coalescence of air bubbles.

Foam masses due to low solids content and limited viscosity are unstable systems. Under the action of surface tension and drainage of liquid, the carcass membrans become thinner and gradually collapse. To give the system more stability immediately after whipping, the mass is mixed with hot sugar syrups containing structurants (agar, agaroid or pectin). During cooling of the shell, the foam frame becomes semi-rigid. Special types of structurants of different brands have been developed in order to obtain appropriate types of marshmallows, for example, pectin-based mass is characterized by thixotropy, ie restoration of structure after mechanical action and lack of syneresis observed in whipped products on agar. Depending on the method of molding, pastille products are divided into cut (marshmallow) and jigging (zefir) [45,46].

Zefir. The technology is based on the use of low-esterified pectin, which allows to expand the range of sugar confectionery with a foamy gelatinous structure [47].

Apple puree weighing 281.24 kg is mixed with 6.45 kg of sodium lactate, 14.83 kg of low-esterified pectin, 304.03 kg of white sugar, 61.39 kg of egg protein, 7.88 kg of lactic acid, 0.47 kg of vanilla essence and whipped the resulting mixture for 13… 15 minutes under a pressure of 0.2 MPa, at the end of whipping added sugar molasses syrup weighing 554.53 kg, which boiled with 330.14

kg of white sugar and 187.17 kg of molasses to a solids of 83… 85% and a temperature of 75… 80 ° C, formed products in the form of hemispheres, kept for 2… 5 hours at a temperature of 20… 25 ° C, connected the halves, sprinkled with powdered sugar weighing 29.75 kg, wrapped and packed.

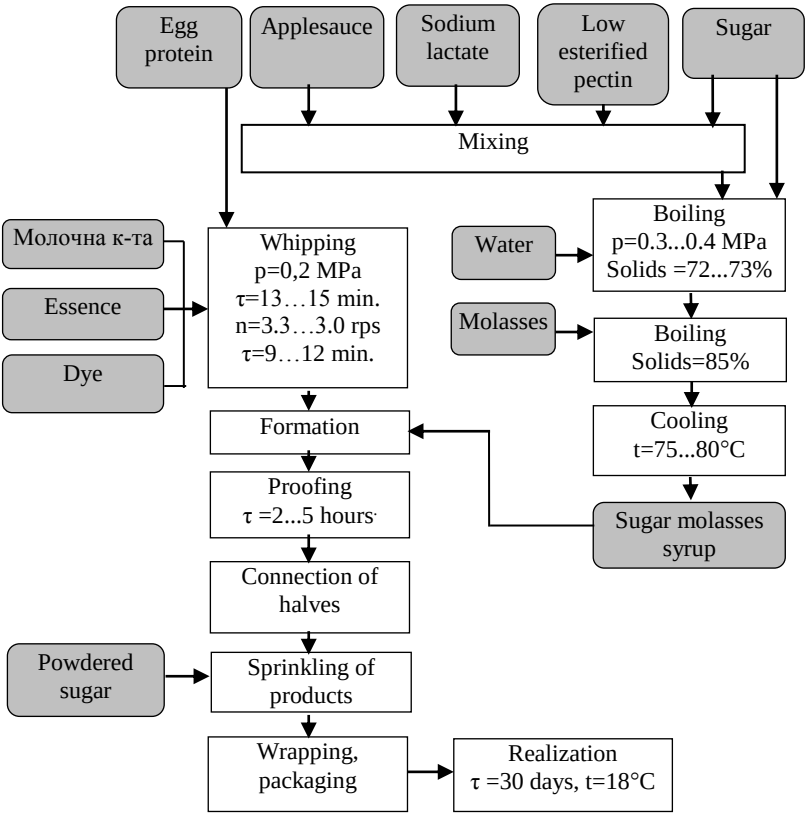


Figure 3.6 - Technological scheme of zefir production

Marshmallow. Obtaining a marshmallow based on low-esterified pectin in the form of fine powder, which was not used in the confectionery industry, provides an expansion the range of sugar confectionery products with a foamy jelly-like structure such as marshmallow, use new functional raw materials, reduce energy consumption and increase technological efficiency. [49].

Apple puree weighing 639.24 kg is mixed with 492.64 kg of white sugar, 24.45 kg of egg protein and whipped the resulting mixture for 10… 12 minutes, at the end of whipping added sugar-pectin-molasses syrup weighing 348.61 kg, cooked from 225.42 kg of white sugar, 7.09 kg of low-esterified pectin, 59.32 kg of molasses and at temperature 85… 95 ° C, after this added 6.27 kg of lactic acid, 0.63 kg of vanilla essence, mixed, formed a layer, kept for structure formation, cut into cubes, sprinkled with powdered sugar weighing 45.87 kg, dried in the first stage for 2.5… 3 hours at an air temperature of 40… 45 ° C and humidity of 40… 45%, for the second - 2 hours. at a temperature of 50… 55 ° C and humidity of 20… 25%, cooled, wrapped and packed.

The technology of marshmallow using apple pectin concentrate has been developed [48].

Production of lokum (Turkish delight) and fruity whipped candies. The range of confectionery products with a foam structure is quite diverse, however, candies and oriental sweets have a special place in it, traditionally in great demand among the population.

Whipped confectionery masses in their general form are dispersed systems. They are obtained by pre-whipping part of the recipe mixture, thus forming a thick foam with microscopically small air bubbles surrounded by a thin membrane of viscous fruit-protein-sugar mixture. Under the action of the surface tension force, the individual bubbles in the foam mass connect, increasing in size, as a result of which the degree of dispersion decreases, increasing in size, as a result of which the degree of dispersion decreases, the foam decreases. To prevent this process in the composition of the membrane,which wraps the air bubbles, added the surfactant, usually egg protein.

Conducted research suggest that it is possible to replace egg protein up to 30% of the prescription amount with a 10% solution of low-esterified pectin (LEP) while maintaining the volume of product output and increase the stability of foam systems.

Sugar-starch-molasses syrup, the specific weight of which in the prescription mixture is 70 ... 75%, determines the initial viscosity of the technological mass, which, in turn, determines the necessary conditions for obtaining foam. The addition of LEP to the prescription composition changes the physicochemical parameters of the obtained foam, which necessitates the determination of rational

ratios of starch, sugar and LEP to ensure the desired viscosity. The optimal concentration of starch and sugar for lokum and fruity whipped mass (semi-finished product for candies), which provides high quality products, is expressed respectively by the ratio (11.0...11.5): (70.0...70, 5): (9.0...9.5): (55.0...55.5).

The influence of LEP concentration as the main gel-forming component on the viscosity of starch solutions was studied (Fig. 3.6).

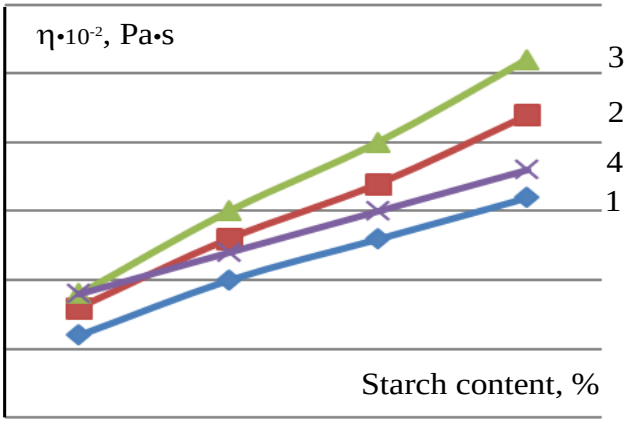


Figure 3.6 - Dependence of the viscosity of the modified starch solution on the LEP concentrations 1- Starch; 2 - Starch + 0.1% LEP; 3 - Starch + 0.2% LEP; 4 - Starch + 0.4% LEP;

Adding LEP to the starch solution changes its properties. Thus, the viscosity for a system containing 11% starch is similar to systems containing 9.6 ... 9.8% starch and 0.1% LEP, 9.0 ... 9.5% starch and 0, 2% LEP, 10.0 ... 10.3% starch and 0.3% LEP.

For a similar 9% system, the viscosity characteristic is identical to the characteristics of the following systems: 8.55 ... 8.6% starch and 0.1% LEP, 8.4 ... 8.45% starch and 0.2% LEP, 8.45 ... 8.5% starch and 0.3% LEP.

As a result of studies of the strength of jellies, it can be stated that the most rational ratios of starch: sugar: LEP for lokum is (9.0 ... 9.3) :(68 ... 70): 0.2%, for fruit whipped semi-finished products - (8.3 ... 8.5): (53 ... 55): 0.2%.

The analysis of the data allowed to choose the ratio of prescription components, in which the products have high organoleptic

characteristics, and their physical and chemical parameters are as close as possible to the products made by traditional technology.

Table 3.15 - The effect of low-esterified pectin on the strength of sugar-starch gels

Concentration of LEP, %	Percentage of starch and sugar		Concentration of sugar, %	The amount of starch at 0,2% LEP, %					
	11:70	9:55		9.0	9.3	9.5	8.3	8.4	8.5
0.0	374	296	70	384	392	407			
0.1	415	337	68	370	376	398			
0.2	450	364	66	354	361	376			
0.3	355	289	55 53 51				327 288 266	332 301 287	345 312 304

For lokum, the prescribed amount of starch, sugar and LEP is defined as 9.3: 68: 0.2, for candies - 8.4: 53: 0.2. The amount of molasses and fruit and berry stew, as well as other flavor components is compiled at the level of traditional recipes (table 3.16).

Table 3.16 - Recipes for lokum and fruit whipped candies with the use of LEP

Name of raw materials	Mass fraction of solids, %	Raw material consumption per 1 ton of finished product, kg			
		lokum		fruit whipped candies	
		in reality	in solids	in reality	in solids
White sugar	99.85	552.0	551.2	572.33	571.47
Powdered sugar	99.85	57.1	57.0	-	-
Potato starch	80.0	83.5	66.8	90.39	72.31
Molasses	78.0	113.6	88.6	115.24	89.89
Blackcurrant stew	69.0	63.5	43.8	55.16	38.06
Egg protein	12.0	20.0	2.4	35.6	4.27
LEP	90.0	2.0	1.8	2.0	1.8
Citric acid	98.0	4.3	3.9	5.81	5.3
Essence	-	0.2	-	-	-
Total		896.2	815.5	1074.02	762.97
Finished product output		1000.0	778.0	1000.00	750.00

Lokum (Turkish delight). The technology is based on the use of LEP as a structurant [55].

The proposed method of obtaining lokum includes mixing LEP with white sugar, apple puree, boiling the system to 74… 76% of solids, whipping for 5… 7 minutes to obtain a system with a foam-like structure, mixing with citric acid, forming the finished mass (laying on trays with a layer of 25 mm by smearing), keeping at a temperature of 20…25 ° C for 3…4 hours for structuring, drying, cutting the layer into bars of size 20×25×40 mm, sprinkled with powdered sugar with vanilla and packaging.

The chemical composition of the proposed product is slightly different from the traditional one. The change in the mass fraction of solids for lokum is 2.0...2.2%, for candies - 3.0%; the content of reducing sugars decreases by 0.9...1.3%, the acidity does not actually change.

The technology of lokum production (Fig. 3.7) with the use of LEP includes the stages of preparation of raw materials, preparation of a LEP solution and starch-sugar-molasses syrup, whipping mass, proofing and forming products, wrapping and packaging.

Preparation of raw materials is carried out in accordance with the technological instructions for the production of oriental sweets. Starch-sugar-molasses syrup is prepared in a cooking machine. The starch is combined with white sugar and dispersed in water at a temperature not exceeding 40 ° C in a ratio of starch: water 1:10. The mixture is boiled under a pressure of 0.3...0.4 MPa to a dry matter content of 72...73%. At the end of boiling added molasses.

Starch-sugar-molasses syrup, cooled to 75...80 ° C, egg protein mixed with a solution of LEP (ratio of LEP and water is 1: 9) is fed into the whipping machine, and whipped for 7...8 minutes. At the end of whipping, added blackcurrant stew, citric acid and essence and continue whipping for 2...3 minutes.

The finished mass is fed to the formation, poured into trays and left in the workshop for 18...20 hours. After proofing, the whipped mass is sprinkled with powdered sugar and cut into bars measuring
40×40 mm. After cutting, sprinkled with powdered sugar, wrapped, packaged and stored.

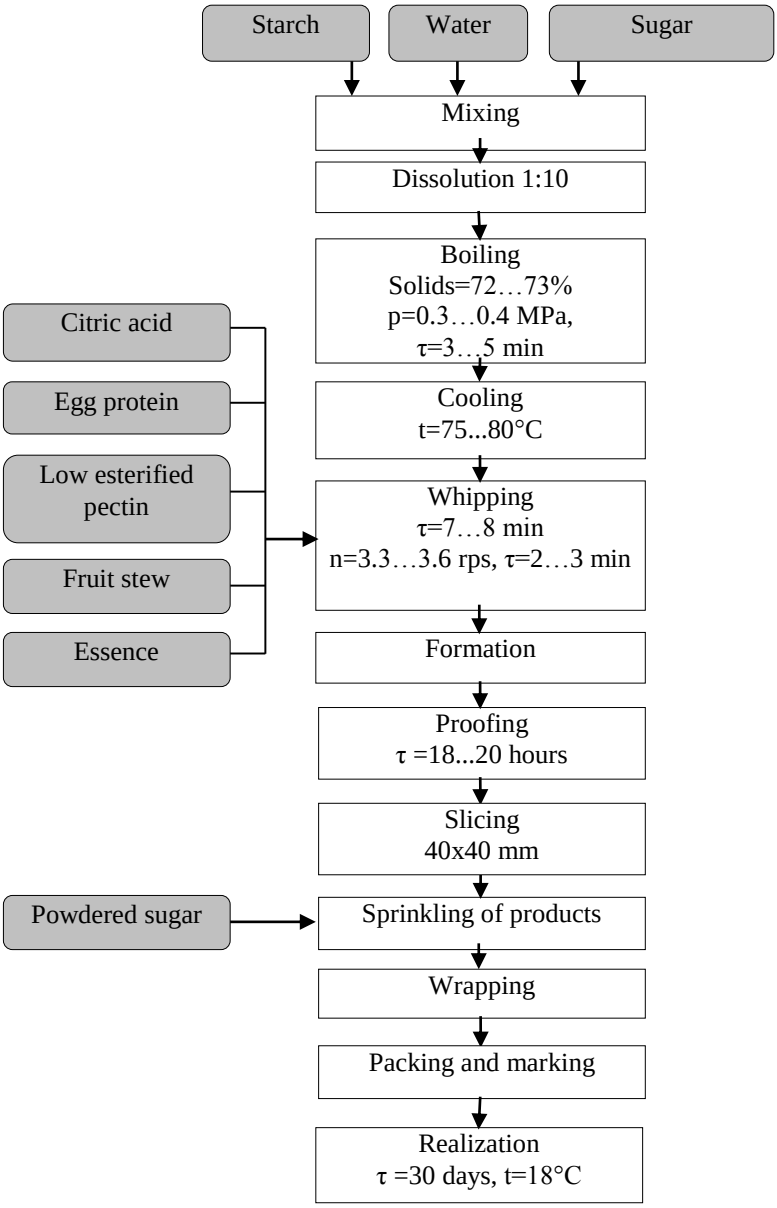


Figure 3.7 - Technological scheme of lokum (Turkish delight)

Technology of production of fruity whipped candies (Fig.3.8) The technology includes stages of raw materials preparation, preparation of LEP solution and starch-sugar-molasses syrup, preparation of whipped mass, formation of housings, glazing of candies, cooling, wrapping, packing and marking [50].

Preparation of a LEP solution, starch-sugar-molasses syrup and whipped mass is similar to the processes described above for lokum. The finished whipped mass is poured into trays and left in the workshop for 18... 24 hours. After proofing, the mass is removed from the trays, covered with a thin layer of chocolate or fat glaze. In 60 ... 90 minutes cut into individual candies, dried for 1 ... 1.5 hours and sent for additional glazing.

Cooling of glazed candies takes place in a cooling cabinet: for fat glaze t = 6 ... 8 ° C within 6 ... 7 minutes; for chocolate glaze t = - 8 ...- 10 ° C for 4 ... 5 minutes

Products made according to the developed recipes and technologies are stored for 1 month under the conditions recommended for these types of products (20 ° C). Physicochemical parameters of products are determined. Their values correspond to the norms, namely: for lokum - humidity 19 ... 20%, mass fraction of reducing sugars - up to 40%, total acidity - not less than 0.2%; for candies on the basis of fruit-whipped semi-finished product - humidity 22 ... 25%, mass fraction of reducing sugars - up to 25%, total acidity - not less than 0.35%.

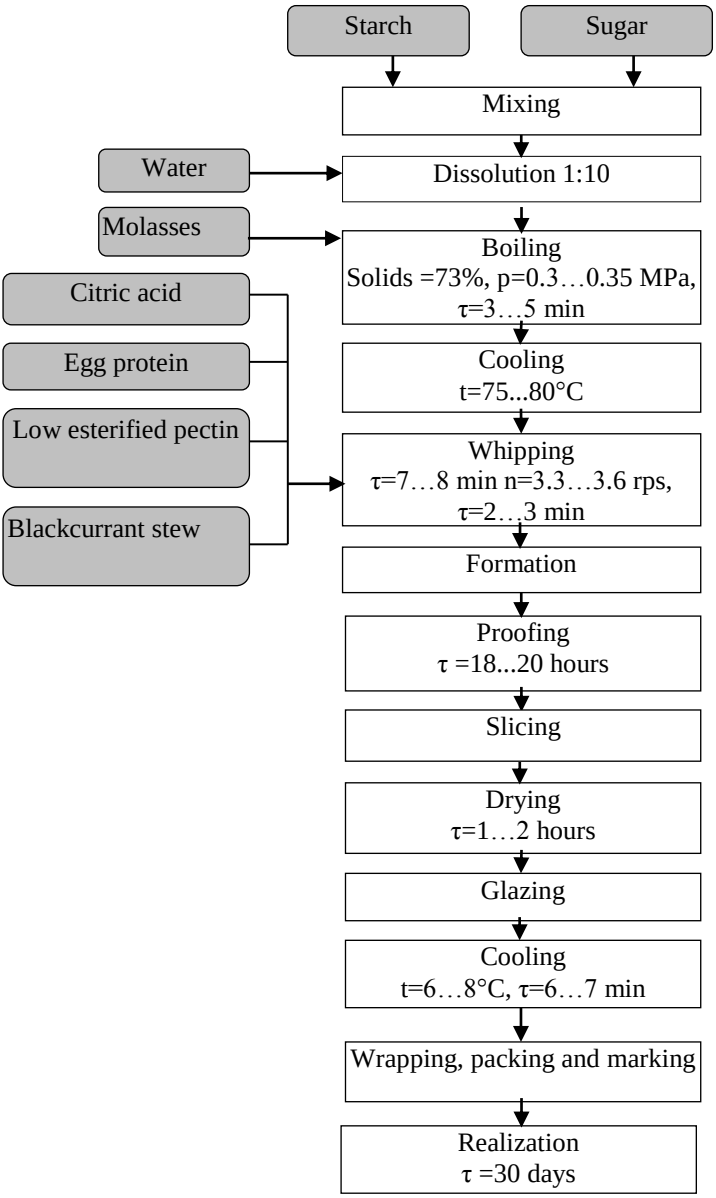


Figure 3.8 - Technological scheme of fruity whipped candies production

The proposed recipes and technologies of lokum and candies using LEP make it possible to reduce the egg protein content to 20% of the total weight of the product without compromising the organoleptic and physicochemical parameters of the product, increase the stability of whipping systems, and thus ensure high product quality.

Candies.

Recipes of candies made by coextrusion “Zolota sopilka” (RC 18 Ukraine 222-K-98), “Charivni brvy” (RC 18 Ukraine 221-K-98) with the use of pectin-containing purees, desserts and powders have been developed. Candies "Shchedryk smak" (RC 18 Ukraine 219-K-98) and "Shchedryk smorodymka" (RC 18 Ukraine 220-K-98) are made with the addition of pectin-containing raw materials and extrusion products, candied fruits, nuts [52,53].

The technology of "Tsytrusovi" candies is based on the use of low-esterified pectin, which helps to expand the range of sugar confectionery products with a jelly-like structure such as candy. Preparation of "Tsytrusovi" candies includes stages of mixing dissolved in water low-esterified pectin, sugar, molasses, citrus stew, malic puree and lactic acid, boiling the mass to a solids content of 75%, pouring into molds, keeping 1.0… 1.5 hours for jellies formation, extraction, chocolate glazing, cooling and packaging [51].

Jelly-like semi-finished products for flour confectionery. On the basis of the conducted researches of functional-technological properties of pectin-containing purees, juices the assortment of thermostable fillings, jelly glaze is developed and the technology of their production is scientifically substantiated: on the basis of carrot hydrolyzed puree (CHP) - filling "Karotynka", carrot-apple hydrolyzed puree (CAHP) - filling "Karotynka-yabluko", pumpkin hydrolyzed puree (PHP) - filling "Harbuzynka"; on the basis of carrot pectin-containing juice (CPJ) - jelly glaze "Karotel" and developed recipes (Tables 3.17, 3.18, 3.19, 3.20) [87–92].

Table 3.17 - Recipe of the filling "Karotynka"

Name of raw materials	Mass fraction of solids, %	Raw material consumption, kg			
		on download		per 1 ton of finished products	
		in reality	in solids	in reality	in solids
Carrot hydrolyzed puree	11.0	54.7	6.02	746.35	82.1
Sugar	99.85	39.6	39.54	540.04	539.23
Low-esterified apple pectin	90.0	0.5	0.45	6.82	6.14
Modified starch	87.0	4.5	3.92	61.45	53.5
Citric acid	91.2	0.58	0.53	7.93	7.23
Calcium citrate	90.0	0.12	0.11	1.66	1.5
Total		100.0	50.57	1364.25	689.70
Output	68.0	73.09	49.87	1000,00	680,00

Table 3.18 - Recipe of the filling "Karotynka-yabluko"

Name of raw materials	Mass fraction of solids, %	Raw material consumption, kg			
		on download		per 1 ton of finished products	
		in reality	in solids	in reality	in solids
Carrot hydrolyzed puree	11.0	33.0	3.63	430.87	47.40
Apple hydrolyzed puree	10.0	19.0	1.90	248.08	24.81
Sugar	99.85	42.4	42.34	553.64	552.82
Low-esterified apple pectin	90.0	0.5	0.45	6.53	5.88
Modified starch	87.0	4.5	3.92	58.83	51.18
Citric acid	91.2	0.48	0.47	6.73	6.14
Calcium citrate	90.0	0.12	0.11	1.60	1.44
Total		100.0	52.82	1306.28	689.67
Output	68.0	76.59	52.08	1000.00	680.00

Table 3.19 - Recipe of the filling "Harbuzynka"

Name of raw materials	Mass fraction of solids, %	Raw material consumption, kg			
		on download		per 1 ton of finished products	
		in reality	in solids	in reality	in solids
Pumpkin hydrolyzed puree	11.0	57.0	6.27	824.67	90.71
Sugar	99.85	41.5	41.44	600.45	599.55
Low-esterified apple pectin	90.0	0.8	0.72	11.57	10.42
Citric acid	91.2	0.6	0.55	8.72	7.96
Calcium citrate	90.0	0.1	0.09	1.45	1.30
Total	-	100.0	49.07	1446.86	709.94
Output	70.0	69.1	48.38	1000.00	700.00

Table 3.20 - Recipe of the jelly glaze "Karotel"

Name of raw materials	Mass fraction of solids, %	Raw material consumption, kg			
		on download		per 1 ton of finished products	
		in reality	in solids	in reality	in solids
Carrot hydrolyzed juice	8.5	35.0	2.98	395.09	33.58
High-esterified apple pectin	90.0	0.6	0.54	6.76	6.09
Low-esterified apple pectin	90.0	0.6	0.54	6.76	6.09
Sugar	99.85	43.4	43.33	489.04	488.30
Citric acid	91.2	0.3	0.27	3.34	3.05
Molasses	78.0	20.0	15.6	225.40	175.80
Calcium citrate	90.0	0.1	0.09	1.13	1.01
Total	-	100.00	63.35	1127.52	713.92
Output	70.00	88.73	62.11	1000.00	700.00

New types of semi-finished products with a jewel-like structure were presented at the professional competitions "Sweet Triumph - 2011" and "Sweet Triumph - 2012" in the XVII and XVIII

Specialized Exhibitions of Confectionery and Bakery Industry "SWEETS & BAKERY Ukraine" and received awards "Triumph of Innovation" for filling "Karotynka-yabluko", jelly glaze "Karotel"

Technological scheme of production of fillings on the basis of carrot, carrot-apple, pumpkin hydrolyzed purees provides preparation of raw materials for production, preparation of fillings, their cooling and packing (Fig. 3.9).

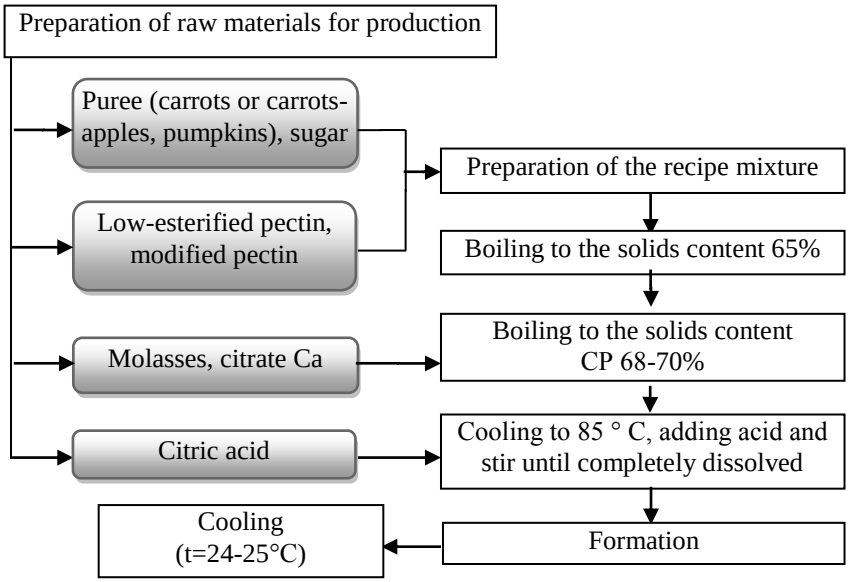


Figure 3.9 - Technological scheme of preparation of fillings on the basis of carrot, carrot-apple, pumpkin hydrolyzed purees

Preparation of raw materials. The sugar is sifted through a sieve with holes with a diameter of not more than 3 mm and passed through magnets to remove metal impurities.

In the preparation of fillings used carrot, apple, pumpkin hydrolyzed puree, made in accordance with TS U 15.3 - 35422486 - 002: 2009 "Fruit puree, vegetable, fruit and vegetable". The puree is filtered through filters with a hole with a diameter of not more than 2 mm.

The gelling ability of pectin is pre-tested by the laboratory. In the case of using pectin, which is well soluble in water and does not require pre-swelling in water, prepare a mixture of pectin-sugar. To prepare a dry mixture for each weight part of pectin take 3… 5 parts by weight of white sugar, all this is thoroughly mixed. Spent on the preparation of a dry mixture of sugar is subtracted from the total prescribed amount of sugar.

Citric acid is dissolved in water in a ratio of 1: 1 and filtered through a thin cloth or several layers of gauze.

Preparation of filling. Pectin-containing puree is mixed with sugar, pectin or a mixture of pectin and modified starch, which are dosed according to the recipe in the appropriate amount by weight of the puree.

When preparing the filling on the basis of CHP, the ratio between CHP and sugar is 58:42, the amount of LM pectin ARA 300FB is 1.0% by weight of the filling.

When preparing the filling on the basis of CAHP, the ratio between CHP, AHP and sugar is 35:20:45, the amount of LM pectin ARA 300FB is 0.5%, the amount of MK Pregel 200 G - 4.5% by weight of the filling.

When preparing the filling on the basis of PHP, the ratio of PHPand sugar is 58:42, the amount of pectin is 0.8% by weight of the filling

The prepared mixture is boiled to a solids content of 65%, then added calcium citrate in an amount of 0.2% to the filling based on CHP, 0.12% based on CAHP, 0.1% to the filling based on PHP and boiled the mass to a solids content 68… 70%. When the mass has cooled to a temperature of 80-85 ° C, added citric acid and mixed thoroughly again.

The finished filling is formed into prepared containers such as "Bag-in-box", disposable of polymeric materials or barrels with aseptic bags-tabs and cooled to 24… 25 ° C. Shelf life of the filling 12 months.

The technological scheme of production of jelly glaze on the basis of hydrolyzed carrot juice provides preparation of raw materials for production, preparation of glaze, its cooling and packing (fig. 3.10).

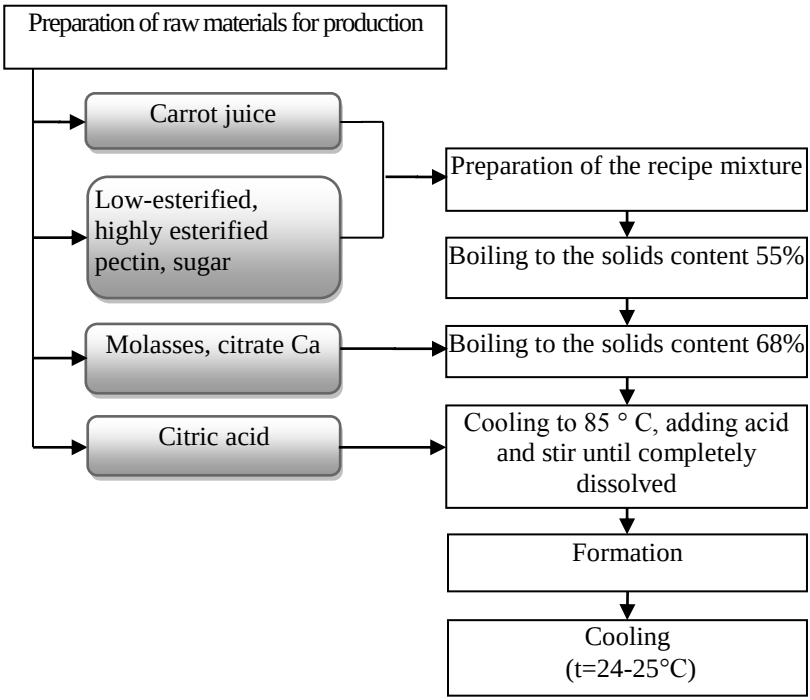


Figure - 3.10 Structural technological scheme of jelly glaze preparation on the basis of carrot pectin-containing juice

Preparation of raw materials. The sugar is sifted through a sieve with holes with a diameter of not more than 3 mm and passed through magnets to remove metal impurities.

Carrot hydrolyzed juice without pulp was used in the development of jelly glaze technology, which is produced in accordance with TS U 15.3-35422486-001: 2009 "Juices, nectars, juice-containing fruits, vegetables, fruity-vegetable , vegetable-fruity" [163]. CHJ is filtered through filters with a hole diameter of not more than 2 mm.

The molasses is heated to 45 ° C and filtered through filters with a hole with a diameter of not more than 2 mm.

The gelling ability of pectin is pre-tested by the laboratory. To prepare a dry mixture for each weight part of pectin take 3…5 parts by weight of white sugar, all this is thoroughly mixed.

Citric acid is dissolved in water in a ratio of 1:1 and filtered through a thin cloth or several layers of gauze.

Preparation of jelly glaze. According to the scheme, a pre-prepared mixture of pectins according to the recipe, mixed with white sugar, is added to the carrot juice and mixed thoroughly until it is completely dissolved.The prepared mixture is served for boiling to a solids content of 55%, then added molasses, calcium citrate and boiled the mass to a solids content of 70%. When the mass has cooled to a temperature of 80…85° C, added citric acid and mix thoroughly again. The finished mixture is formed and cooled to 20…25° C.

The finished semi-finished product is a sturdy jelly with a smooth glossy surface, has a yellow color due to the addition of carrot juice, which eliminates the use of synthetic dyes. Carrot juice gives the products transparency. Such masses retain their shape well and can be used to decorate flour confectionery.

3.11 Technology of jelly dishes using apple pectin concentrate

The range of sweet jelly dishes is quite wide, but special attention is paid to dishes with a foam structure, in particular, sambuc [57].

Sambuc. Sambuc is a dish with high organoleptic characteristics and biological value. In addition, sambuca does not contain exclusively seasonal raw materials and is therefore a universal dish for cooking in restaurants all year round.

High quality indicators of this product are largely determined by the stability of the foam system, which is obtained by whipping the recipe mixture. Sambuc is a homogeneous, loose, fine-porous mass with an elastic consistency. The foamy structure of the dish is provided by pectin substances of fruit raw materials and egg protein, elastic consistency - gelatin. The sucrose content is 18… 20% [59].

In fig. 3.11 shows the technological scheme of sambuc preparation using low-esterified pectin.

In order to expand the range of dietary low-calorie sweet cold dishes with a foamy gelatinous structure, sambuca technology was developed using LEP and sugar substitute - saccharin.

It is known that low-esterified pectins form a jelly-like structure in the presence of calcium ions in a wide range of pH of the technologacal medium with or without adding sugar.

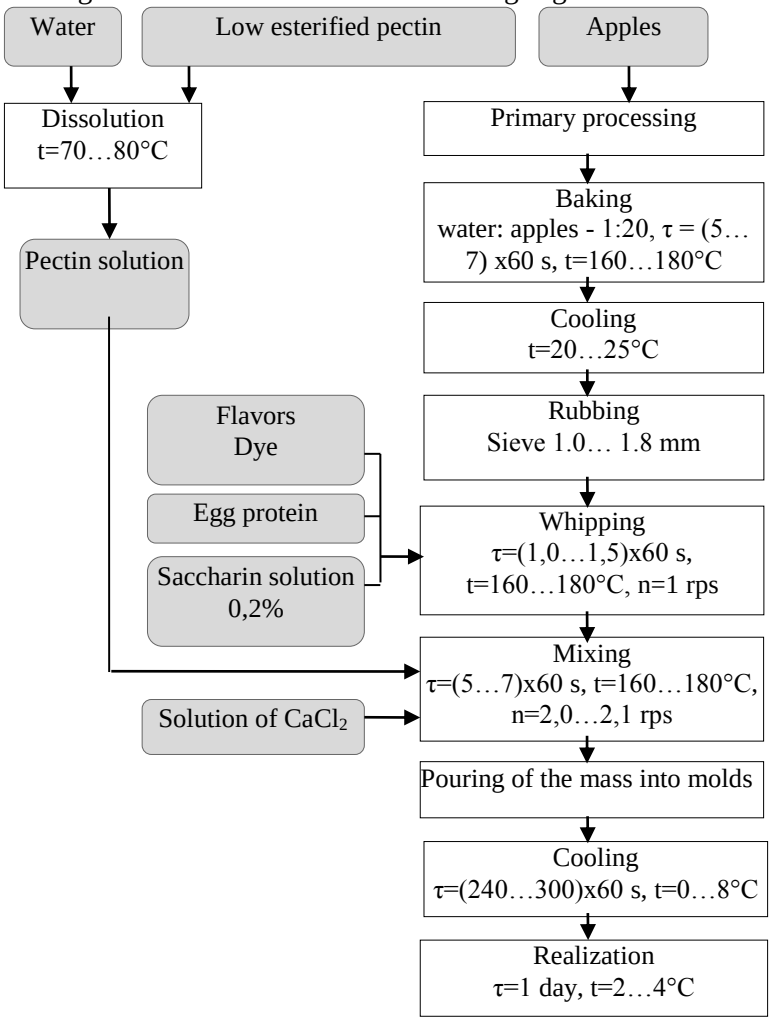


Figure 3.11– Technological scheme of sambuc preparation using low-esterified pectin

According to the developed technology, apple puree obtained from baked apples is cooled, whipped with egg protein, 0.2% saccharin solution, flavoring and dye at a temperature of 35… 40 ° C to form a loose mass. Then a solution of LEP and a solution of calcium chloride are added to the whipped mass in a thin stream with continuous stirring. The mass is poured into molds, cooled and kept for structuring for 3… 5 hours at a temperature of 0… 8 ° C.

Then the sambuc is removed from the molds and watered with fruit syrup. Store the product at a temperature of 2… 4 ° C for one day.

Cream. Obtaining cream based on LEP in the form of fine powder, which has not yet been used in the diet nutrition of restaurants, expands the range of dietary low-calorie sweet cold dishes with foamy gelatinous structure such as cream, the use of new functional raw materials, reducing energy consumption and increasing the efficiency of the technological process by reducing the number of technological stages.

The proposed method of obtaining cream includes mixing LEP with eggs, rubbing the mixture, adding saccharin solution, calcium chloride in the form of a saturated solution, heating to 70… 80 ° C, filtering, adding vanillin, cooling to a temperature of 40… 50 ° C and introducing the obtained mixture with continuous stirring in the cooled and whipped to a loose mass of cream, pouring into molds, cooling to a temperature of 0… 8 ° C, keeping for 3… 5 hours for structure formation, removal from forms [57].

Mousse. The technology is based on the use of apple pectin extract, which allows to expand the range of dietary low-calorie sweet cold dishes with foamy gelatinous structure such as mousse, reduce energy consumption and increase process efficiency by reducing the number of technological stages (mixing pectin with sugar, dissolution). The proposed method of obtaining a mousse includes boiling lemon zest in water for 3… 5 minutes, filtering, adding saccharin in the form of 0.2% solution, powdered LEP, adding squeezed lemon juice, dyes, flavors and saturated calcium chloride solution, cooling to 30… 40 ° C, then whipping until the mixture turns into a loose mass, pouring into molds, keeping for 3… 5 hours at a temperature of 10… 14 ° C for structure formation of the system, removal from molds, watering with cherry syrup [58].

Jelly. Jelly is obtained by mixing apple pectin concentrate with fruit juice or fruit decoction and sugar, boiling the mixture for 3… 5 minutes, then adding dyes, flavors, citric acid, pouring into molds and keeping for 3… 5 hours at a temperature of 20… 25 ° C to form a jelly-like structure. Then the product is removed from the molds and sent for sale [60].

3.12 Technology of dairy pectin products

The role of pectin in dairy production. The group of pectins for the dairy industry includes pectins with different degrees of esterification, which have a constant (standardized) value of susceptibility to calcium in milk, as well as precisely established rheological properties. In particular, the dairy industry uses special pectins to stabilize the structure and extend the shelf life of various dairy products, such as liquid yogurts, puddings, etc. In addition, pectins, as components of fruit jelly fillers, sauces and liquid concentrates, can be used in the production of fruit yogurts, fruit-dairy desserts with fruit fillings.

The properties of dairy products, such as pH, calcium ion concentration, protein and sugar content, especially affect the structure-forming properties of pectins. The main indicators that determine the nature of the action of pectins in dairy products are the degree of esterification and the degree of dissociation of molecules.

The nature of the stabilizing effect of pectins. After mixing a solution of highly esterified pectin with neutral milk, for a short time, it is possible to see the formation of a flaky precipitate of milk proteins, which include casein. At the end of the reaction, the protein flakes together with the smallest droplets of fat form a viscous, thick emulsion, over which is a layer of whey. This process is reversed and does not lead to chemical changes in the composition of casein molecules. In the first scientific publications, such a reaction was called the "pectin phenomenon of milk." The method of protein precipitation with pectin has been used previously, for example, in the production of cheese. Currently, this technology has no industrial significance.

In neutral milk at pH 6.6, casein molecules carry a negative charge and, as a result, repulsive forces predominate between them. This prevents protein deposition. It is assumed that pectin as a strong

hydrophilic compound destroys the protective hydrate shell of casein (Fig. 3.12), resulting in the stability of the latter deteriorates sharply.

When the pH of milk decreases, casein molecules gradually lose negative charges. At the isoelectric point (determined pH value of the product, for casein 4.6) is established almost equal ratio between positive and negative charges. The molecule loses its hydrate shell and at a pH value below the isoelectric point acquires a total positive charge [61, 62].

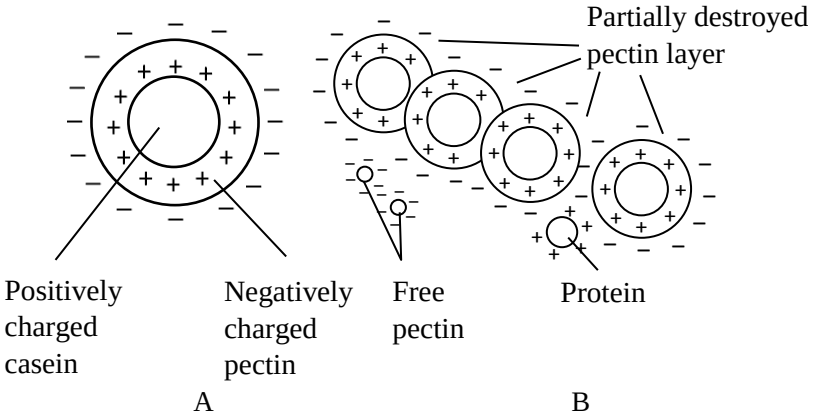


Figure 3.12 - Stabilizing effect of pectin on dairy products A-stabilized casein particle; B - unstable sediment

Negatively charged highly esterified pectins when mixed with a fermented milk product, such as yogurt, interact electrostatically with casein molecules that carry a total positive charge. The formed casein-pectin complex acquires an excess negative charge with a predominance of repulsive forces between molecules. As a result, the interaction of proteins with each other is excluded, as well as the formation of sediment and the separation of whey. The product acquires the so-called physical stability.

Pectins used to stabilize fermented milk products, such as liquid yogurt, must have a high molecular weight and a well-defined degree of esterification - within 70%, as pectins with a lower degree of esterification can react with calcium in milk, and pectin molecules with more with a high degree of esterification have a smaller number of negatively charged carboxyl groups and therefore less reactive.

The dosage of pectin depends on the content of milk proteins. The optimal dosage does not affect the viscosity of the product, an overdose of pectin impairs the taste.

An important factor that ensures the stability of the product is the pH 4. Lowering the pH by 0.5 units leads to a sharp decrease in stability. Thus, the pH value of fermented milk products and their acidity significantly affect the dissociation of pectin and, as a consequence, its ability to interact with calcium ions.

When low-esterified pectins are added to neutral milk, a milk pudding or gel is formed, the consistency of which, depending on the dosage of pectin, can vary from viscous-fluid to strong. Such structures are formed as a result of the interaction of pectin with calcium in milk. It is assumed that the gelling effect is enhanced in the process of additional interaction of pectins with milk proteins.

Low-esterified pectin for neutral dairy products must meet certain requirements. First of all, it must be standardized with respect to the constant value of sensitivity to calcium ions. The commercial preparation of pectin must also contain a certain amount of suitable buffer salts.

When using LEP in the production of fermented milk products, such as yogurt with a stable structure, it is possible increase the strength of milk jelly and prevent the release of whey. It should be borne in mind that as a result of lowering the pH in the process of acidification of yogurt, general changes in salt balance lead to the complete transition of calcium compounds into a soluble form. Thus, the concentration of calcium ions reacting with pectin increases sharply. The formed calcium pectate is precipitated.

Therefore, the high concentration of calcium limits the amount of pectin used. If the dosage of pectin in the product still needs to be increased, the excess activity of calcium ions is reduced by adding buffer substances and, if possible, simultaneously increase the pH.

The process of stabilization of dairy systems is influenced by the following factors:

The pH value of the product. Most fermented milk products have a pH value of 3.8… 4.0. Pectins have a stabilizing effect in the pH range of 3.5… 4.2. Optimal organoleptic properties of the product can be achieved when working in the pH range of 3.6… 4.0. Therefore, in the case of using in the recipe of yogurt with a low

protein content of a large amount of fruit juice, it is necessary to predetermine the total (titrated) acidity of the juice. To prevent a decrease in the stability of the product, ie the separation of whey, it is recommended to use fruit juices, the acidity of which is equal to or greater than the acidity of yogurt.

At pH values below 3.5, pectins cannot stabilize the product. This is due to a sharp decrease in the degree of dissociation of carboxyl groups of pectin at a pH below 3.5, which, in turn, causes a decrease in the degree of interaction of pectin with casein molecules. At pH above 4.0, the stabilizing effect is also reduced. It is not recommended to work at a pH higher than 4.2, which in some cases can lead to an undesirable increase in viscosity due to the increased degree of dissociation of pectin molecules..

The amount of pectin used to stabilize the dairy product is also affected by the acidity of the fruit juice (if used). Fruit juice with a low total acidity adversely affects the stability (there is a risk of serum separation) of the finished product. To correct this negative effect, it is necessery to increase the dose of pectin.

Milk protein content. It has been empirically established that for satisfactory stabilization of milk yogurt with a protein content of 4%, it is sufficient to use 0.5% pectin in terms of weight of the finished yogurt. At higher concentrations of milk proteins it is necessary to increase the dosage of pectin by an appropriate amount.

In cases of low milk protein content, it is possible to reduce the dosage of pectin, which may be disproportionate to the concentration of milk protein. So, for example, it is established that at 1% content of milk proteins the minimum admissible level of dosage of pectin from 0,15% to 0,25% is reached.

Particle size of milk proteins. In the process of microbiological acidification of milk (maturation, cultivation of yogurt) a number of technological parameters determine the particle size of milk proteins. As noted above, the stabilizing effect is achieved by adsorption of pectin on the surface of milk proteins. Adsorbed pectin gives all particles a single electrostatic charge, which leads to repulsive forces between individual particles.

For optimal stabilization of milk protein particles with very small sizes, more pectin is required in order to bind a significant area of adsorption of the protein surface. At the same time, very large

protein particles also require a significant amount of pectin to keep them in equilibrium (suspended) state.

Increasing the dosage of pectin can be carried out to the level of 0.7% in terms of weight of the finished product.

Products "Pectoline", "Petolact" and drink "Pectynovyi". Technologies and recipes of dairy products with the addition of pectin, produced on the basis of secondary raw milk, have been developed. Their organoleptic characteristics are given in table 3.21.

Table 3.21 - Organoleptic characteristics of dairy pectin products "Pectoline", "Petolact" and drink "Pectynovyi"

Indicators	Characteristic		
	"Pectoline"	**"Petolact"**	**"Pectynovyi"**
Appearance and consistency	Homogeneous liquid with disturbed or undisturbed clot, slight viscosity and slight serum separation are assumed	Homogeneous liquid-drink, with the consistency of kissel, the system - dessert	Homogeneous liquid-drink
Taste and smell	Pure sour milk with the taste and aroma of the filler	Sweet and sour, like whey, with the taste and aroma of the filler	Sweet and sour, like whey, with the taste and aroma of the filler
Color	Creamy, uniform throughout the mass	Light brown, uniform throughout the mass	Characteristic of the filler

"Pectoline" is made from skim milk or buttermilk and pectin concentrate. Pasteurized milk raw material and prepared pectin concentrate are mixed and fermented with a leaven consisting of separately cultured mesophilic lactic acid streptococcus, acidophilic bacillus and kefir leaven. Fermentation is carried out at a temperature of 32 ± 2 ° C to a clot acidity of 85 ° T. The duration of fermentation

is 6 ... 8 hours. At the end of fermentation, the product is cooled, mixed and packaged in consumer containers.

The basis of the product "Petolact" is a mixture of whey with skimmed milk and pectin concentrate, to which sugar and starch are added. The filtered whey and skimmed milk are pasteurized and cooled. The starch is dissolved in chilled skim milk. The whey is mixed with pectin concentrate, heated to 65 ... 70 ° C, added white sugar, heated to 90 ° C and enter the dissolved starch. The mass is withstanded for 5 ... 10 minutes. Thoroughly mixed and cooled product is packaged.

The recipe of the drink "Pectynovyi" includes whey, pectin, sugar and aromatic additives. Pectin is thoroughly mixed with sugar in a ratio of 1: 1, filled with the prescribed amount of water at a temperature of 40 ... 45 ° C and left for 3 ... 4 hours to swell the pectin by periodically stirring the mixture. Then in the mixture with stirring entered the filtered whey, heated to a temperature of 90 ° C, added a filler (syrup), cooled and served for bottling [63,64].

Sour milk paste "Lali" (TS U 18019595-30-96) is made from pasteurized skimmed or normalized milk by fermentation with leaven and subsequent separation of whey with the addition of pectin, salt, spices and greens to the protein base. Depending on the mass fraction of fat, paste "Lali" is made low-fat, 2.5; 5.0; 10.0% fat. The leaven is prepared using pure cultures of thermophilic lactic acid bacteria. The milk is fermented for 4 ... 6 hours to obtain a clot with an acidity of 80 ... 90 ° T. Pressing takes place at a temperature of 8 ... 12 ° C to a mass fraction of moisture 80 ... 89% depending on the fat content of the final product. Fillers are added to the pressed paste [65, 66].

The product has a sour-milk spicy-salty taste with a hint of spices of spices, garlic, greens. Due to the preservative properties of salt, as well as the presence of pectin and spices in the product, the guaranteed shelf life of Lali paste is 10 days.

3.13 Technology of pectin-containing powders

The main source of dietary fiber is plant material, in particular, secondary plant resources: bran of cereals, pomace of fruits and berries, etc. Beet bagasse - a waste of sugar production - is of interest as a source of dietary fiber. Bagasse consists mainly of polysaccharides: cellulose, hemicellulose and pectin substances. The content of pectin substances in beet pulp is up to 30% by dry weight and they are presented in the form of an insoluble form of protopectin. Pectin substances are currently one of the most studied - and as a component of plant cells, and as a dietary supplement, and as a substance that can be attributed to the treatment and prevention and essential for the human body.

As a food additive, pectins are used to thicken, stabilize, shape food; their biological effectiveness (the ability of high- and low-esterified pectins, as well as products containing them, to form insoluble complexes with lead, strontium, cesium, ruthenium and other heavy and radioactive metals, toxins and remove them from the body; positively affect metabolism, state of the cardiovascular system and digestive organs) allows them to be classified as dietary supplements. All these properties are inherent in beet pectin.

Researches on creation of polysaccharide functional complexes from beet bagasse for reception of dietary and food additives are carried out. In order to obtain water-soluble pectin, beet bagasse was subjected to acid-thermal hydrolysis and dried. Such a polysaccharide complex has increased moisture retention, complexing and sorption capacity. When adding it to semi-finished products (puree, paste, powder), the preconditions for the production of dietary, food additives and products with multifunctional properties are created [70].

Pectin-containing powders are obtained from apple, carrot pomace and beet bagasse. The raw material is processed in a solution of food grade acids. After pressing the pomace or bagasse is dried at a temperature not exceeding 90 ° C and crushed (Table 3.22) [67,68].

Table 3.22 - Physico-chemical parameters of pectin-containing powders

Indicator	Norm
Mass fraction of moisture,%, not more	8
Mass fraction of pectin,%, not less	6
Mass fraction of powder in the passage of the sieve at 250 μm,%, not less	80
Mass fraction of metal impurities,% not more	$3.0 \cdot 10^{-4}$
Mass fraction of mineral impurities,%	not allowed
Mass fraction of ash insoluble in 10% hydrochloric acid,%, not more	3.0

Pectin-containing powders are used as an additive in various food products in order to enrich them with dietary fiber. In addition, the powders have a high moisture holding capacity, and their introduction into the confectionery and bakery products allows to increase the shelf life.

Dry pectin-containing mixtures "Pectosan" are prepared by mixing pectin, pectin-containing powders or dry pectin extract with sugar or glucose and citric acid and can be produced in the form of powder, granules, tablets, pills. The mixtures are intended for direct use for prophylactic purposes. The pectin content in the product is up to 12%. Studies conducted at the Dnipropetrovsk Medical Academy have shown that when using a "Pectosan" mixture based on beet pectin powder, heavy metals bind at the level of the gastrointestinal tract and help reduce the amount of xenobiotics that pass through the body and are fixed in tissues. The use of mixtures as a dietary supplement improves intestinal motility, promotes the excretion of heavy metals, pesticides, radionuclides, lowers blood cholesterol [69, 70, 71, 72]

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