MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
Sumy National Agrarian University
State Biotechnological University
National University of Food Technologies

I. KRAPIVNYTSKA, V. LADYKA, M. IANCHYK,
S. OMELCHENKO, O. MELNYK, F. PERTSEVYI

SCIENTIFIC AND PRACTICAL ASPECTS OF PECTIN AND PECTIN PRODUCTS

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Reviewers:

M. Kravchenko, Doctor of Technical Sciences, Professor, Kyiv National University of Trade and Economics;

L. Kapreliants, Doctor of Technical Sciences, Professor, Odessa National Academy of Food Technologies

Collective of authors:

Krapivnytska I., Ph.D., Associated Professor, National University of Food Technologies;

Ladyka V., Doctor of Agricultural Sciences, Professor, Sumy National Agrarian University

Ianchyk M., Ph.D., Associated Professor, National University of Food Technologies;

Omelchenko S., Ph.D., Associated Professor, State Biotechnological University;

Melnyk O., Ph.D., Associated Professor, Sumy National Agrarian University

Pertsevoy F., Doctor of Technical Sciences, Professor, Sumy National Agrarian University

Krapivnytska I.

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The monograph substantiates and develops modern, highly efficient functional technologies with the addition of pectin and pectin products.

Pectin is a natural polysaccharide that combines the properties of a structuring agent and a biologically active compound. Structural formation in products with pectin is manifested in the ability to form strong gels, give stability to emulsions, thicken food masses. The biological activity of pectic substances is expressed in detoxifying, radioprotective, antioxidant, hypoglycemic, immunostimulatory effects. This gives grounds for its widespread use in the creation of health products, preventive nutrition and dosage forms.

This 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

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 sectors 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 products, health products, in 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 abroad is developing rapidly, improving pectin technology from various secondary plant raw materials.

The Ukrainian pectin market is focused on imported supplies. There is no pectin production in Ukraine.

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 is especially needed now by the processing industry of the agro-industrial complex of Ukraine. The production of pectin and pectin products meets these requirements to the greatest extent.

Based on this, it is important for the development of the pectin industry of Ukraine to conduct a set of theoretical and experimental studies to scientifically substantiate and develop modern, highly efficient technologies of pectin and pectin products.

Development of food products, including functional ones, with the addition of pectin and pectin products is an important factor in reducing a number of diseases in the population.

1 TECHNOLOGIES OF PECTIN PRODUCTS FROM PLANT RAW MATERIALS: APPLE PECTIN CONCENTRATE, LIQUID PECTIN, DRY PECTIN EXTRACTS, PECTIN-CONTAINING PUREE

The domestic food industry is focused on the use of pectin as a gelling agent in the production of jelly confectionery and canned goods for mass consumption, for which highly esterified apple and citrus pectin is traditionally used. Pectin is widely used in the production of products for preventive and health purposes, such as beverages, dairy, bakery, etc., consumed daily, and in which pectin is used as a structuring agent, detoxifier, complexing agent, that is, there are no high requirements for gelling ability [1, 3, 4, 5, 6, 7].

In the production of pectin foods there is the dissolution of dry pectin in water, juices, which is a labor-intensive operation, because pectin has a high hygroscopicity, forms lumps on contact with water [2]. The stage of pectin dissolution can be eliminated, and the costs of pectin producers and consumers can be significantly reduced due to the production of pectin extracts from various raw materials. Similar to liquid fruit and vegetable extracts due to manufacturability - the possibility of using hydraulic vehicles, storage in containers, ease of dosing, etc., pectin extracts are widely used in the food industry [43, 44, 59].

The application of hydrolytic nutrients (electroactivated water, citric, lactic, orthophosphoric acid, etc.) makes it possible to use pectin extracts as independent products for prophylactic purposes, as well as food additives in the production of consumer goods. Therefore, the composition of pectin extracts is subject to the following requirements:

- pectin extracts must not contain substances of toxic, carcinogenic, mutagenic or other harmful effects on the human body;

- according to the numerical values of safety criteria, the extracts must meet the indicators for beverages, and must not exceed the permissible levels of toxic elements, microbiological contamination;

- pectin extracts must contain such quantity of pectin and such quality that would allow them to be used as a food and biologically active additive [57].

1.1 Classification of pectin extracts

- Depending on the type of raw material, pectin content and purpose, pectin extracts are divided into:

- - by type of raw material: apple; citrus; fruit and berry; beet; carrot.

- - by pectin content: extract type A (pectin content 0.5 ... 1.0%); extract type B (pectin content 1.1 ... 2.0%); concentrate (pectin content 2.0 ... 4.0%); dry extract (pectin content 10 ... 40%).

- - by purpose: food additive (as a structurant of food technological environments in the production of bakery, dairy, confectionery, canned goods, etc.); dietary supplement (as a radioprotectant and detoxifier, for preventive and health products); when creating dosage forms and pharmaceuticals; for the production of cosmetics and detergents.

1.2 Extractive substances of pectin-containing raw materials

When extracting pectin substances from plant raw materials, other water-soluble substances are extracted from it: carbohydrates, proteins, starch, organic acids, polyphenols, dyes, macro- and microelements, which are ballast relative to pectin, but increase the biological value of pectin products. [16].

The main part of plant cell juice is carbohydrates (glucose, fructose, sucrose and other oligosaccharides).

Up to 30% of cell juice remains in the raw material after pressing. In addition, in the process of hydrolysis of protopectin there is the destruction of molecules of starch, hemicelluloses, cellulose, resulting in the formation of soluble carbohydrates, the composition and amount of which depend on the type of plant. For example, fresh apple pomace contains 6.0 ... 8.0%, in the process of hydrolysis their number increases to 6.7 ... 8.3%. Pre-washing of apple pomace before hydrolysis reduces the dry matter content in the raw material to 2.0%, carbohydrates to 0.7% [20].

Depending on the type of plants, they are dominated by certain carbohydrates: glucose is contained in significant quantities in grapes, plums, raspberries; fructose - in grapes, apples, pears, black currants; sucrose - in sugar beets, apricots, citrus fruits, carrots. This causes a variety of mono - and disaccharides of pectin extracts.

The amount of protein in fruit and vegetable crops is insignificant (in currants - 1.0%, plums - 0.2%; rowan - 1.4%, apricots - 0.9%) and most of them are enzyme and membrane systems. In the process of acid-thermal treatment of raw materials is the denaturation of proteins, the permeability of plant tissue increases and some proteins are extracted from raw materials [9, 11, 12, 14].

Starch is contained in pectin-containing raw materials in small quantities and a significant part of it is hydrolyzed during heat treatment. In pectin extracts - 0.1 ... 0.5% starch.

Together with pectin-containing substances, polyphenols are extracted from plant raw materials: anthocyanins, leukoanthocyanidins, catechins. Their content in plant raw materials depends on the type of plant: anthocyanins are contained in chokeberry (50 mg%), black currants (610 ... 920 mg%), cherries (250 ... 330 mg%); leukocyans - in sea buckthorn (240. ..260 mg%), apples, rowan; catechins are found in large quantities in apples, rowan. The presence of polyphenols in pectin extracts due to enzymatic oxidation reactions leads to darkening of both the extracts and pectins. The presence of some flavonoids (naringin in citrus) and

terpenoids (in citrus) causes a bitter taste of fruits and products of their processing, including pectin extracts.

Pectin-containing raw materials contain and extract organic acids: the most common malic (0.7 ... 1.3%) in apples; citric - 1% in currants, 5.7% in lemons; tartaric (0.3 ... 1.7%) is in the grapes. Their content in raw materials determines its acidity. Active acidity (pH) for fruits is pH = 3 ... 4, for vegetables pH = 4.5 ... 6. Acidity determines the taste and affects some technological processes: hydrolysis, gelation, sterilization, etc. The presence of acids in liquid and dry pectin extracts causes a sour taste, increases shelf life.

Vitamins contained in plant raw materials have different qualitative and quantitative composition, even for plants of the same species. However, in the technological processing of raw materials are destroyed and contained in pectin extracts in small quantities.

Extraction of pectin is accompanied by the extraction of macronutrients (K, Ca, Mg, Fe, P, S, Na) and trace elements (Cu, Mn, Mo) from plant raw materials. They are distributed unevenly in the fruit. Thus, the core of apples contains several times more Ca, K, Mg and P than the pulp, so their content in pectin extract will be higher than in juices. Some of the macro - and microelements are contained in plants in the form of salts of organic acids (phytates, oxalates, etc.). Some Ca^{2+} and Mg^{2+} ions are part of protopectin and are released during hydrolysis, passing into pectin extract. The amount of minerals in the product determines the ash content, which in the pectin extract is 0.1 ... 1.0%. The ash content in pectin and pectin products determines the effectiveness of the purification of pectin extracts and pectin.

At the same time, the organoleptic characteristics of pectin extracts (taste, smell) from fruit raw materials improve with increasing degree of extraction of cell juice from raw materials, which allows to use them as a beverage, as well as for the production of blended beverages for general use. At the same time the nutritional value of products increases.

1.3 Chemical composition and organoleptic characteristics of pectin extracts

The nutritional and biological value of pectin extracts and dietary products based on them is determined by their chemical composition. Studies of the chemical composition of pectin extracts obtained under industrial conditions have shown that they contain, in addition to pectin, carbohydrates, organic acids, crude protein and other substances (table 1.1).

Pectin extracts are a homogeneous viscous liquid that has a sour, characteristic taste and smell from raw materials, from light gray, yellow to brown colour. The main physicochemical parameters are presented in table. 1.2.

The quality indicators of dry pectin extracts obtained by drying concentrated extracts in a spray dryer are presented in table.1.3.

Table 1.1 – **Chemical composition of pectin extracts**

Indicators	**Apple extract**	**Beet extract**	**Citrus extract**
Mass fraction of pectin substances, %	0,88	0,71	0,95
Mass fraction of sugars, %	1,07	0,91	1,28
Mass fraction of "crude" protein, %	0,19	0,16	0,12
Organic acids, % in terms of citric acid	0,32	0,17	0,55
Vitamins	traces	traces	traces

Table 1.2 – **Physico-chemical parameters of pectin extracts**

Indicators	Apple		Citrus		Beet		Carrot	
	Extract	Concentrate	Extract	Concentrate	Extract	Concentrate	Extract	Concentrate
Mass fraction of soluble solids, %	2,0	6,0	1,8	6,5	1,7	6,6	2,7	7,3
Mass fraction of pectin, %	1,0	3,0	1,2	3,6	1,1	3,5	1,5	3,1
pH	3,0	3,0	3,5	3,5	2,5	2,5	2,8	2,8
The strength of 2% pectin gel by the method of Sosnowski, kPa	53	53	50	50	40	40	30	30
Complexing ability, Pb^{2+}/ml	0,95	1,7	0,8	1,5	3,1	6,6	2,5	2,9

Table 1.3 – **Quality indicators of dry pectin extracts**

Indicators	Extracts		
	Apple	Beet	Citrus
Mass fraction of moisture, %	9,2	9,0	9,4
Mass fraction of pectin, %	41,9	43,2	36,5
PH of 5% solution	3,0	2,8	3,4
Saccharose, %	12,4	10,8	10,8
Mass fraction of "crude" protein, %	7,03	8,3	9,8
Gelling ability, kPa	35,9	20,6	37,2
Complexing ability, mg Pb^{2+}/ g of extract	35,6	153,0	25,6

Mineral and amino acid composition of pectin extracts. Extraction of pectin is accompanied by the extraction of micro- (Cu,

Mn, Zn) and macronutrients (K, Ca, Mg, Fe, Na) from plant raw materials. They are distributed unevenly in plants. Thus, the core of apples contains several times more Ca, K, Mg than the pulp, so their content in pectin extract will be quite high. Most of the micro- and macronutrients are contained in plants in the form of salts of organic acids (eg, sodium phytate). A number of Ca ions are part of protopectin [31, 32, 33] and are released during hydrolysis, turning into pectin extract. The amount of minerals in the product determines the ash content, which ranges from 0.1% to 0.3% by weight of dry pectin extracts.

The content of macro-, microelements, as well as the content of heavy metal ions in dry beet, apple, carrot extracts are given in table. 1.4, 1.5.

Table 1.4 – **Mineral composition of dry pectin extracts**

Pectin extract	**Macro-, microelements, mg/100 g**						
	Mg	**Ca**	**K**	**Na**	**Fe**	**Mn**	**Cr**
Beet	0,20	21	25	9	38	0,0005	0,8
Apple	0,15	8,6	136	18	62	0,0005	0,64
Carrot	ОДО	15	40	25	54	0,0006	0,30

Table 1.5 – **The content of heavy metals in pectin extracts**

Name of extracts	**The content of heavy metal ions, mg/kg**				
	Zn^{2+}	**Pb^{2+}**	**Cu^{2+}**	**Cd^{2+}**	**Hg^{2+}**
Pectin (permissible by standard)	30,0	1,0	10,0	0,1	0,1
Beet pectin extract	2,0	0,7	5,6	0,02	0,02
Apple pectin extract	2,0	0,9	1,2	0,04	0,01
Carrot pectin extract	0,6	0,8	0,4	0,01	0,02

Apple, carrot pomace and beet pulp contain a significant amount of amino acids [15, 16]. In addition, amino acids are formed in the process of hydrolysis of protein substances of pectin-containing raw materials. The amino acid composition of dry pectin extracts was determined (table 1.6).

Table 1.6 – **Amino acid composition of pectin extracts**

The name of the amino acid	Pectin extracts, mg-10/100 mg		
	Beet	Apple	Carrot
1	2	3	4
lysine	20,76	3,12	4,36
histidine	7,99	1,22	1,11
arginine	8,22	1,25	1,67
oxyproline	25,49	—	—
aspartic acid	17,21	18,01	13,66
threonine	14,09	3,45	4,66
serine	15,49	5,98	5,14
glutamic acid	28,50	13,30	28,64
proline	17,08	2,78	5,13
glycine	11,63	4,89	6,19
alanine	13,46	5,38	7,82
cysteine	1,58	1,12	0,26
valine	13,80	1,9	3,94
methionine	1,01	0,64	0,40
isoleucine	4,76	1,43	3,83
leucine	10,20	3,83	5,87
tyrosine	13,97	1,74	2,26
phenylalanine	6,33	2,81	2,17

Amino acid-enriched pectin extracts have a high biological value, and make it possible to use them in the production of food and biologically active additives.

1.4 Apple concentrate technology

In order to organize a comprehensive processing of apples and expand the range of pectin-containing canned products, pectin concentrate technology is of greatest interest to increase the profitability of enterprises for processing fruits and vegetables and raw materials [17, 18, 19, 21].

There are various schemes for producing pectin concentrate using sulfite, lactic, tartaric, citric, orthophosphoric acids or electroactivated water as a hydrolytic factor [5].

Dried and fresh apple pomace is used as a raw material. Preparation of the pomace consist in grinding them to a size of 1.5...2.0 mm and washing with water with a temperature of 20...25 °C within 20...30 min [57].

Hydrolysis of extraction of pectin substances is carried out at the following parameters: temperature - 80...90 °C, pH = 2,8...3,2; the ratio of the mass flow rates of the solid and liquid phases of 2.5...4.0; the duration of the process is 1.0...1.5 hours.

After hydrolysis, the mixture is separated by pressing, decantation and the like. The pectin extract is cooled, clarified, filtered and directed to the concentration to a pectin content of 2.5...3.0 %, followed by aseptic storage.

In enterprises where there are no conditions for aseptic storage, the extract is treated in sulfitators; storage is carried out in enameled containers for 6...9 months.

The concentrate can also be preserved with sorbic acid or its salts (sorbate of potassium or sodium). To do this, at a temperature of 80 °C bring in sorbic acid in an amount of up to 0.1% by weight. Stir for 10...15 min, then the concentrate is cooled to a temperature of 20 °C and sent for storage. The concentrate can be preserved by hot bottling in an airtight glass container.

The technological scheme of production of apple pectin concentrate is shown in fig. 1.1.

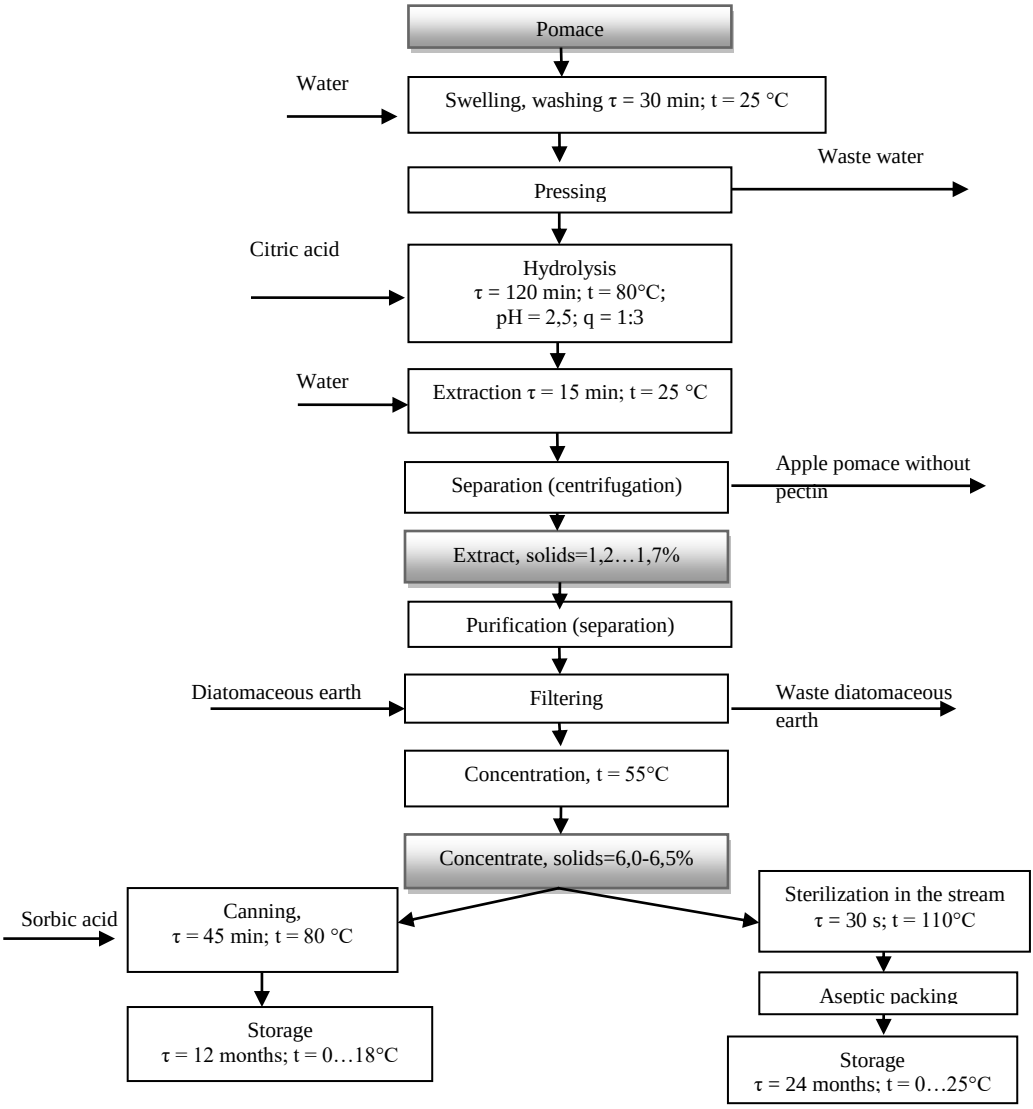

Figure 1.1 - Technological scheme of pectin concentrate production from apple pomace

1.5 Liquid pectin technology

The following pectin-containing raw materials are used for the production of liquid pectin: apple pomace, beet pulp, fruit and vegetable pomace. Various acids are used as hydrolyzing substances: citric, orthophosphoric, lactic, etc.

1.5.1 Investigation of the process of enzymatic deesterification for obtaining low-esterified pectins

The effect of enzymes on pectin. The breakdown of pectin by enzymes is of great practical importance and is widely used in the processing of sugar beet fruit, as well as in the clarification of juices and wines. As is known, under the action of enzymes of the hydrolase class, the reactions proceed according to the following scheme:

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

In the process of enzymatic hydrolysis, an enzyme-substrate complex is formed, which undergoes intramolecular rearrangement under the influence of the active center of the enzyme. The rupture of the anhydride bond of the catalyzing substrate leads to the release from the enzyme-substrate complex of one of the reaction products. The second product is released after rearrangements associated with the addition of a water molecule. In the process of enzymatic hydrolysis of pectin substances involved: pectinesterase, endopolygalacturonase, exopolygalacturonase [35, 62].

Non-hydrolytic cleavage of pectin is channeled by enzymes from the class of pectintranseliminase lyases. Pectolytic enzymes are widespread, they are synthesized by plants, microorganisms, but are absent in animal cells. According to the report of the Commission for the development of enzymes nomenclature, pectolytic enzymes are classified as follows [63].

Pectinesterase (polymethylgalacturonatesterase, enzymes classification (EC) 3.1.1.11) deesterifies pectin with the formation of pectic acid due to the removal of methoxyl groups. Pectinesterases are synthesized by higher plants, microscopic fungi and bacteria. They have a high specificity to the methyl ester of pectic acid. With the gradual demethoxylation of pectin, there is a marked decrease in enzyme activity. Pectinesterase of fungal origin has a high activity at pH 5.0 ... 6.5 and a temperature of 50 ° C for 60 • 60 s.

Endopolygalacturonase (EC 3.2.1.15) hydrolyzes α- (1-4) - bonds of pectic acid in an arbitrary, disordered manner. The enzyme is produced by microorganisms and higher plants. With increasing degree of esterification of pectic acid, the degree and rate of hydrolysis decrease, due to the fact that free carboxyl groups increase the activity of the enzyme. The activity of the enzyme decreases with decreasing chain length of oligogalacturonans.

Exopolygalacturonase (EC 4.2.2.9) hydrolyzes pectin, sequentially cleaving bonds from the unreduced end of the substrate. Fungal exopolygalacturonases show maximum activity at pH 4 ... 6 and form monogalacturonic acid as the final product. The bacterial enzyme from *Erwinia aeroideae* acts at pH 7.2 and the product of catalysis is digalacturonic acid.

There is information about endopolymethylgalacturonase, which hydrolyzes α- (1-4) - pectin bonds. But the existence of this enzyme has not been conclusively proven: there is a possibility that polymethalacturonase is taken as polygalacturonase drugs that contain pectinesterase.

In addition, if the substrate is not completely esterified, the possibility of hydrolysis of pectin by polygalacturonase or polygalacturonate lyase in areas that do not contain methoxyl groups is not excluded.

The class of lyases that act on pectin substances include endo- and exopolygalacturonatelyase, polymethylgalacturonatelyase.

Endopolygalacturonatelyase (EC 4.2.2.2) performs a disordered, arbitrary cleavage of pectic acid bonds in the transelimination reaction. The optimal pH value = 8.0 ... 10.0. One of the main features of pectolyticlyases is their activation by calcium ions.

Exopolygalacturonatelyase (CF 4.2.2.9) sequentially cleaves pectic acid from the unreduced end of the substrate molecule in the transelimination reaction. For these enzymes, the optimal pH values = 8.0 ... 9.5.

Endopolymethylgalacturonatelyase causes arbitrary cleavage of pectin during transelimination. It is the only known enzyme that directly hydrolyzes pectin. The main producers are fungi and a small number of bacteria. Depending on the producer, the pH optimum effects of enzymes range from 5.5 to 8.3. The best substrate for endopolymethylgalacturonatelyase is highly esterified pectin. Polygalacturonic acid and pectic acid amide are not hydrolyzed by the enzyme. Endopolymethylgalacturonatelyase activity decreases rapidly with decreasing chain length.

Pectolytic enzyme preparations are widely used in food industries for maceration of plant raw materials, reduction of viscosity of juice concentrates, clarification of juices, etc.

For pectin production it is important to prevent the action of factors of enzymatic destruction of pectin substances. For the preparation of pectin-containing raw materials it is possible to use enzyme preparations released from pectolytic enzymes.

Enzymatic method of obtaining low-esterified pectin (LEP) is based on the specific action of the enzyme pectinesterase, which catalyzes the hydrolysis of ether bonds of pectin [22, 23, 24, 25, 26].

Obtaining LEP having a molecular weight close to the molecular weight of native pectin, determines the choice of source of pectinesterase with a minimum content of polygalacturonase complex, the result of which is the rupture of L-1,4-bonds in the polyuronide molecule. In plants, polygalacturonase is rare and in small quantities, so many foreign companies offer highly purified

and homogeneous pectinesterase preparations from plant raw materials, despite the fact that its release from plants is complicated by strong adsorption by plant tissues. So the firm Sigma (USA) offers different types of pectinesterase preparations from tomatoes and oranges. However, due to the limitations of the raw material base, plants cannot be industrial sources of enzymes. In addition, pectinosterases of plant and microbial origin differ in their properties and mechanisms of action.

Microbial pectinesterases are more thermostable than plant ones. The optimal pH value of pectinesterases of higher plants is in the alkaline zone in the range from 7 to 9, fungal - in the acidic range from 3.5 to 7.

A fast and easily controlled method of obtaining apple LEP involves the concentration of pectin extract simultaneously with the deesterification of tomato pectinesterase. Comparative studies of fungal and plant pectinesterases have been conducted abroad. They convincingly show the benefits of fungal esterases. It is emphasized that samples of pectins de-esterified by fungal pectinesterases, as well as samples of pectins de-esterified by alkali, have a uniform distribution of charge density of free carboxyl groups and are characterized by the degree of counterion binding, which increases with increasing charge density.

In samples of pectin deesterified by plant pectinesterases, the degree of binding of Ca^{2+} ions was independent of the degree of esterification. The reason for this is the lateral distribution of free carboxyl groups, due to which dimers are formed.

Analysis of pectin deesterification methods shows that the undeniable advantage of the alkaline deesterification method is the high reaction rate. However, given the fact that the alkaline deesterification rate of depolymerization increases with increasing temperature faster than the rate of deesterification, to obtain high-quality samples of LEP requires careful control of temperature and pH. But even with all the process parameters set depending on the composition of the processed material, the degradation of the pectin

macromolecule cannot be avoided and the pectin obtained by alkaline deesterification is characterized by a lower molecular weight compared to the original.

Caustic alkalis in the process of deesterification act not only as a catalyst, they are spent on the neutralization of carboxyl groups released. In this regard, to maintain the speed of the process at a constant level requires continuous additional application of alkali. In addition, significant amounts of acids are required to neutralize the reaction mixture and remove pectin-bound ions. All this leads to a significant increase in the cost of reagents compared to other methods of deesterification. The main disadvantage of the acid method of reducing the degree of esterification is the low speed of the deesterification process.

The product of acid deesterification differs in its structure from pectin obtained using alkalis. In an acidic environment, the glycosidic bond in the galacturonide molecule is much more stable than the glycoside bond of neutral polysaccharides included in the pectin molecule. As a result, in acid hydrolysis the bonds between the polyuronide chain and the branches of neutral saccharides that are part of the pectin macromolecule are destroyed. At the same time, the accompanying neutral polysaccharides undergo hydrolysis [13, 39, 40].

The most promising way to reduce the degree of esterification of pectin is the use of microbial pectinesterases. The pectins obtained with their use are devoid of the disadvantages characteristic of pectins obtained by plant pectinesterases and due to the lateral arrangement of free carboxyl groups. Currently, the widespread use of enzymatic hydrolysis to reduce the degree of esterification of pectin is hindered by the lack of industrial preparations of microbial pectinesterase, which have sufficient purity, as well as the lack of detailed ideas about the processes of enzymatic deesterification.

A study of the enzymatic de-esterification of apple pectin using the enzyme preparation of the company DSM (Netherlands) (Fig. 1.2).

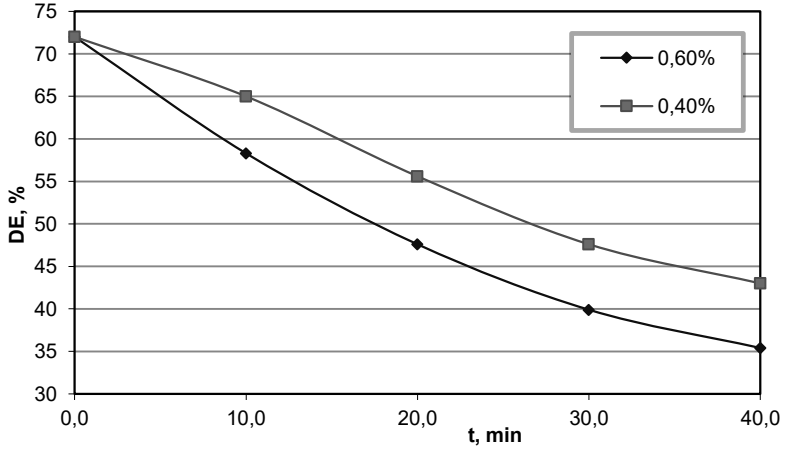

Figure 1.2 - Dependence of changes in the degree of esterification of pectinon the duration of the enzymatic deesterification process
(concentration of enzyme preparation 0.4%, 0.6%)

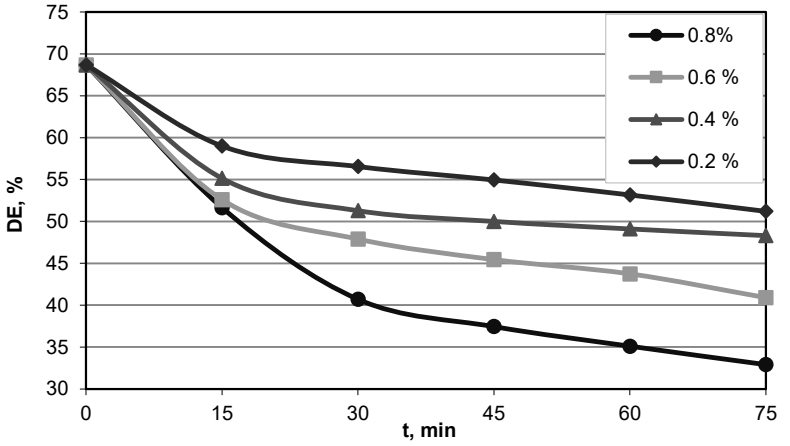

Figure 1.3 - Dependence of changes in the degree of esterification of pectin on the concentration of the enzyme preparation of pectinesterase

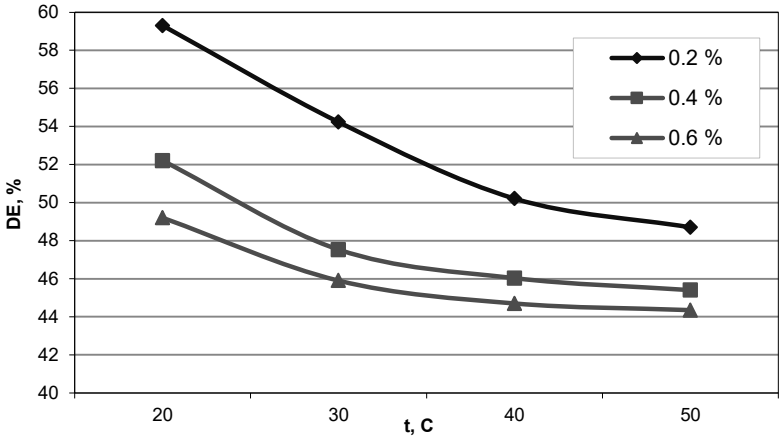

Figure 1.4 - Dependence of the degree of esterification of pectin on the temperature of the deesterification process

1.5.2 *Technological scheme of liquid pectin production*

Technological scheme of liquid pectin production includes the following stages (Fig. 1.5):

Washing of raw materials. Pectin-containing raw materials from the warehouse enters the shop and is loaded into the washing tank with a stirrer. Washing is carried out with drinking water with a temperature of 20… 25 ° C at a ratio of raw materials and water of 1: 3 for 30 minutes, after which it is fed to the belt press by a screw mezgon pump.

Pressing. The raw material is fed to the belt press, where the wash water is removed from the raw material to a solids content 25… 28%, by auger conveyor is fed into the storage tank.

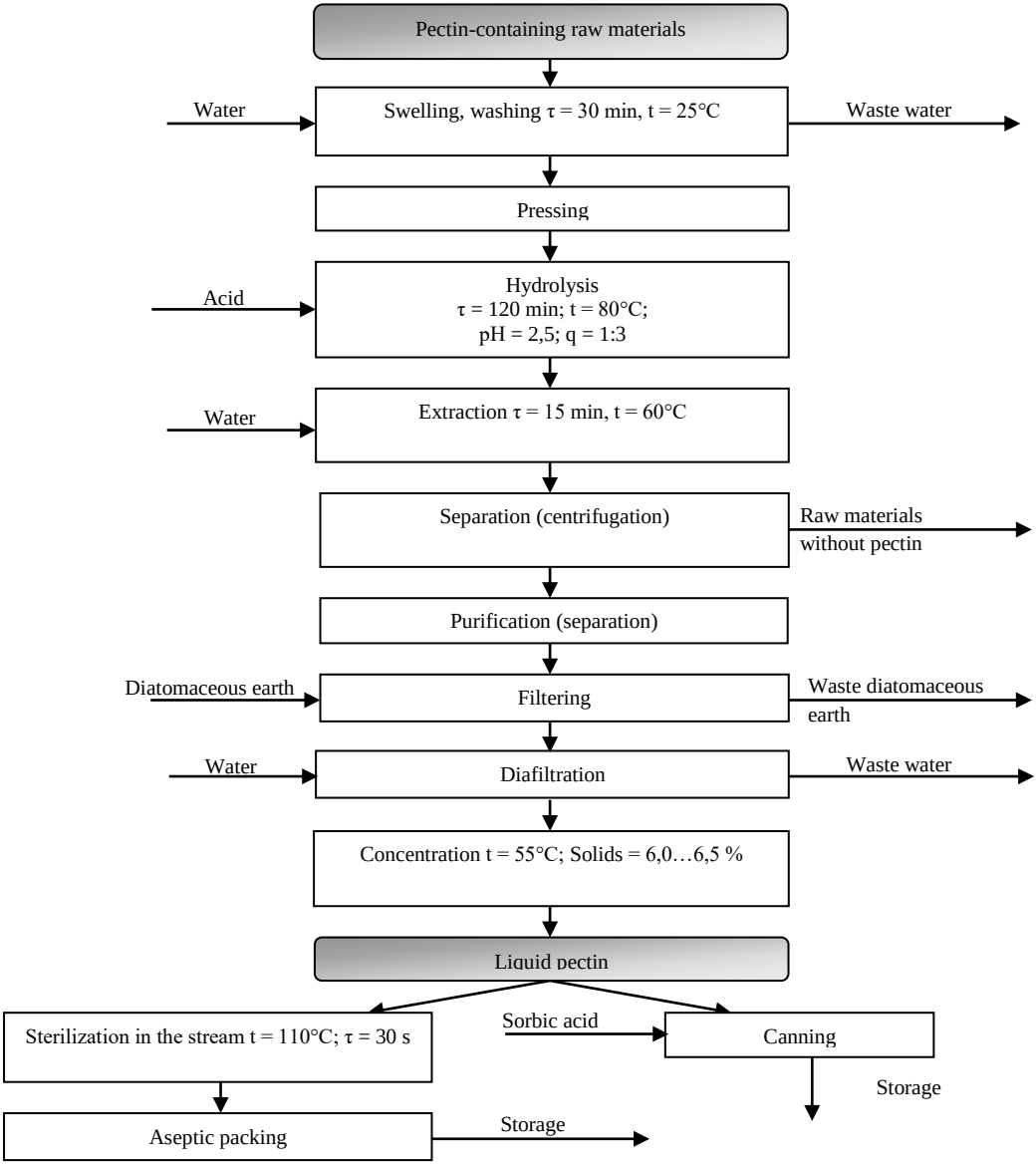

Figure 1.5 - Technological scheme of production of liquid pectin

Hydrolysis-extraction. The process of hydrolysis of protopectin and extraction of pectin substances is carried out in a hydrolyzer with a stirrer.

Hydrolysis-extraction of pectin substances is carried out with periodic stirring with the addition of acid solution to the raw material (at a ratio of 1: 3).

At the end of loading the reagents, the hydrolyzer is sealed and the process of hydrolysis-extraction of pectin substances is carried out at the following parameters: pH = 2.5… 3.2; process temperature 75… 80 ° C; the ratio of pomace and acid solution is 1: 3; duration of hydrolysis-extraction process 120 min.

After the hydrolysis-extraction process, the mass is pumped to the separation centrifuge.

Separation of hydrolysis mixture. To separate the extract, the hydrolysis mixture is fed to a continuous centrifuge. After centrifugation and removal of pectin, the raw materials are sent for neutralization with further use as cattle feed, and the pectin extract is sent to the tank. Qualitative indicators of pectin extract after centrifugation: solids content - 1,2 ... 1,7%; content of PS (pectin substances) - 0.5%; pH = 2.8… 3.2.

Separation of pectin extract. The pectin extract from the tank is pumped into a separator for cleaning. The sediment formed as a result of separation is sent for disposal. The clarified extract from the separator is fed into the tank, and then pumped to the diatomaceous earth filter.

Extract filtration. The process of filtering the pectin extract is carried out on a diatomaceous earth filter. The filtered extract is sent to the tank.

Concentration of the extract. The extract is concentrated on a vacuum evaporator to a solids content = 6.0… 6.5%, the concentration of precipitated pectin substances 2.5… 3.5%, the pH of the extract is 1.7… 2.2. Concentration takes place at 55 ° C for 2 hours. The vacuum on the vacuum evaporator is formed by the condensing head. The extract is evaporated under vacuum. After

evaporation, the liquid pectin enters the tank, where it is pumped for aseptic preservation or preservative preservation.

Preservation of liquid pectin with sorbic acid. From the vacuum evaporator, pectin is fed into a tank with a stirrer and a jacket with a usable volume of 10 m³. The estimated (0.05… 0.1%) amount of sorbic acid is added to pectin. The mixture is stirred for 45 minutes until complete dissolution of the preservative. The liquid pectin is then fed into a storage vessel, having previously cooled it in a heat exchanger.

Packing of liquid pectin in an aseptic installation. The concentrate is sterilized in a stream for 30 s at a temperature of 110 ° C and packed in plastic bags, which are placed in plastic or metal barrels with a volume of 200 liters.

1.6 Technology of dry pectin extracts

The application of dry pectin extracts provides an opportunity to increase the production of pectin-containing products, expanding their range, reduces the cost of dry pectin for food production (bakery, pasta, canned food, beverages) [57, 59, 61, 62].

1.6.1 *Investigation of hydrolysis process of raw materials for the production of pectin extracts*

Extraction of pectin substances from plant raw materials includes several parallel processes: hydration of raw materials with simultaneous addition of reaction catalysts - protons and hydrolysis of protopectin with the formation of water-soluble pectin substances and extraction of water-soluble pectin.

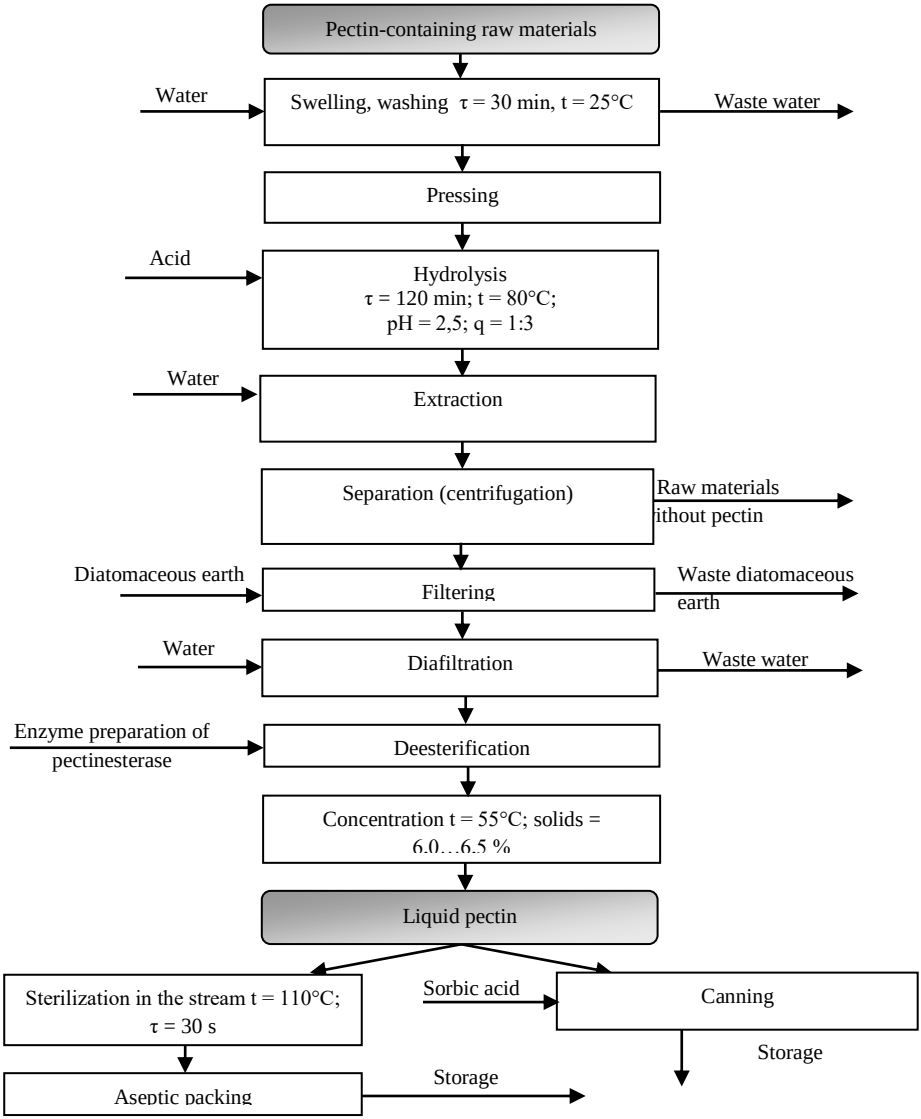

Figure 1.6 - Technological scheme of production of low-esterified liquid pectin

Based on the main provisions of hydrolysis and its conditions and taking into account the requirements for the quality of pectin extract, conducted research on the process of hydrolytic cleavage of protopectin of apple, carrot pomace and beet pulp preparation of raw materials.

Hydrolysis of protopectin is an internal process and depends on the temperature, duration of the process and the pH of the medium [27, 28, 29, 30]. The hydrolysis process does not depend on the ratio of the solid and liquid phases and raw material particle shapes [34, 35, 36]. Depending on the preparation and depth of hydrolysis of pectin-containing raw materials changes the molecular weight of pectin, the degree of esterification, as well as its ability to gelation and complexation. To achieve the maximum degree of hydrolysis ($C_г$) can be changed the temperature, pH and duration of the hydrolysis process

It is established that with increasing temperature increases not only the degree of hydrolysis, but also the speed of the process [40]. Thus, when the temperature changes from 70 ° C to 80 ° C, the hydrolysis constant increases approximately three times, the maximum degree of hydrolysis - at 90 ° C. However, at this temperature, the quality of pectin deteriorates due to thermal destruction of pectin [39].

Studies have been conducted to determine the degree of hydrolysis of various raw materials. Hydrolysis took place under a vacuum of 0.75 atm at constant values: pH of the medium 2.1, at a temperature of 80 ° C and the duration of the process - 120 minutes The degree of hydrolysis of protopectin with citric acid with a concentration of 2.0%, corresponding to a pH of 2.1, was investigated. In order to determine the optimal technological regime of the hydrolysis process, apple, carrot pomace and beet pulp were used, which are subject to preliminary heat treatment (Fig. 1.7).

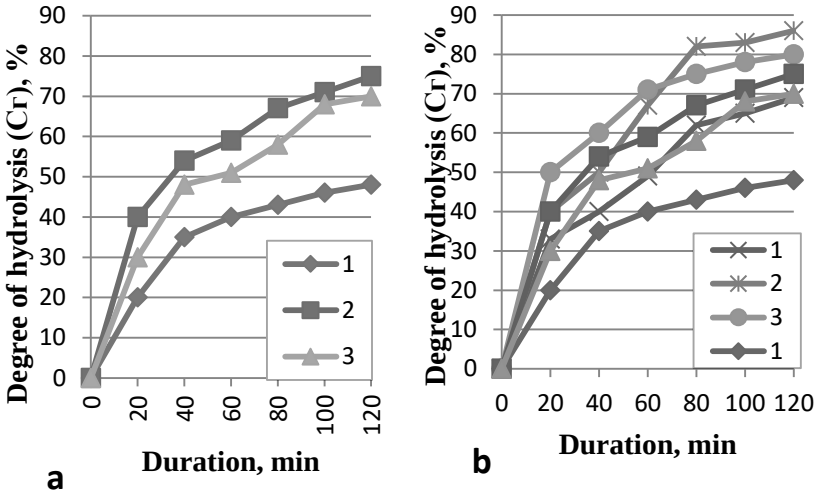

Figure 1.7 - Dependence of the degree of hydrolysis of the prepared raw material with citric acid on the duration of the process at t=80 °C and pH 2,1:

a - washed; *b* - washed and blanched; 1- beet; 2- apple; 3- carrot.

To preserve the quality indicators of pectin, reduce the duration of the hydrolysis process and ensure greater yield of pectin, it is advisable to prepare raw materials, including washing and blanching.

The results show that depending on the level of raw materials preparation increases not only the degree of hydrolysis, but also the speed of the process. To obtain an extract with high quality hydrolysis process must be carried out at pH = 2.1 ... 3.0, which meets the requirements of food.

Analysis of the curves of the hydrolysis degree for each raw material shows that the hydrolysis takes place differently (Fig. 1.7, a). Thus, the lowest degree of hydrolysis has beet pulp - 48%, the highest - apple pomace - 75% and carrot pomace - 70%. This is due to the relevant quality characteristics of raw materials.

To increase the degree of hydrolysis, it is necessary to reduce the pH of the medium. Phosphoric acid was used as a hydrolytic factor. Hydrolysis of carrot raw materials with a mixture of phosphoric acid with a concentration of 1.5% and citric acid with a concentration of 2%, corresponding to a pH of 1.8, and raw beet - phosphoric acid with a concentration of 2%, corresponding to a pH of 1.5 was carried out. The hydrolysis process lasted 120 minutes under boiling conditions under vacuum.

Under such conditions, the degree of hydrolysis reaches 69% and 79% for beet and carrot raw materials, respectively, which satisfies the requirements of the process. In fig. 1.8, 1.9, 1.10 show the change in the degree of hydrolysis of prepared beet, apple, carrot raw materials during the process of hydrolytic cleavage of protopectin by different acids.

The results of studies of hydrolysis of protopectin of carrot and beet prepared raw materials with a mixture of food acids of different concentrations show that the most effective use of a mixture of acids with a concentration of 1.0% citric and 0.5% phosphoric. At this ratio of acids, the degree of hydrolysis of protopectin for carrot raw materials is 89%, and for beet - 86%.

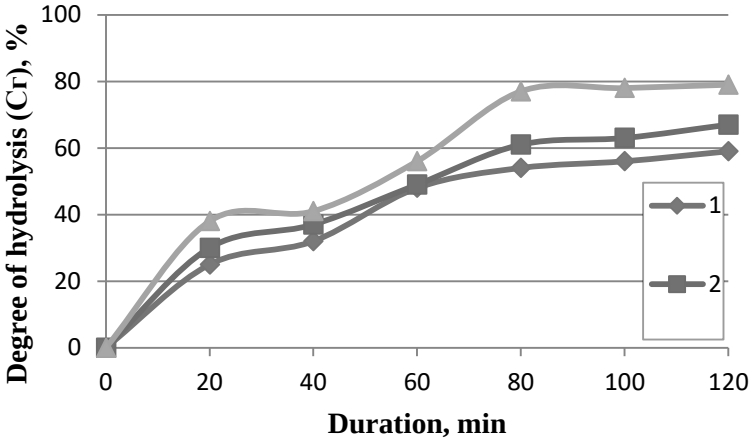

Figure 1.8 - Dependence of the hydrolysis degree of the prepared beet raw material on the duration of the process of pectin hydrolytic cleavage of : 1 - citric acid; 2 - a mixture of lemon and phosphorus in a ratio of 1: 0.5; 3 - phosphoric acid.

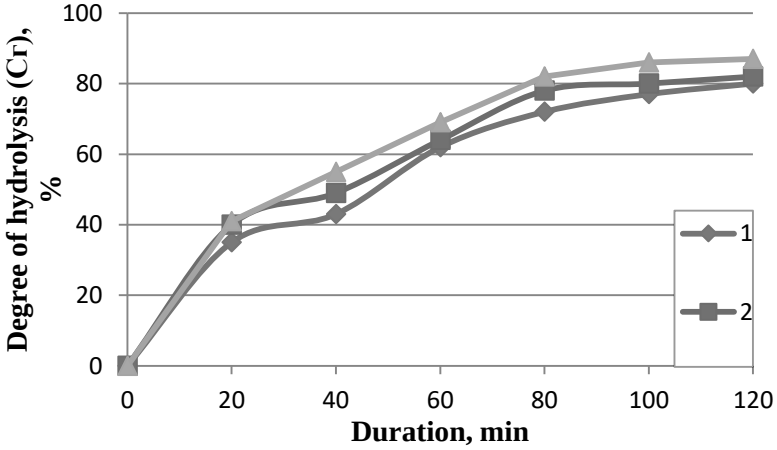

Figure 1.9 - Dependence of the hydrolysis degree of the prepared apple raw material on the duration of the process of pectin hydrolytic cleavage of : 1 - citric acid; 2 - a mixture of lemon and phosphorus in a ratio of 1: 0.5; 3 - phosphoric acid.

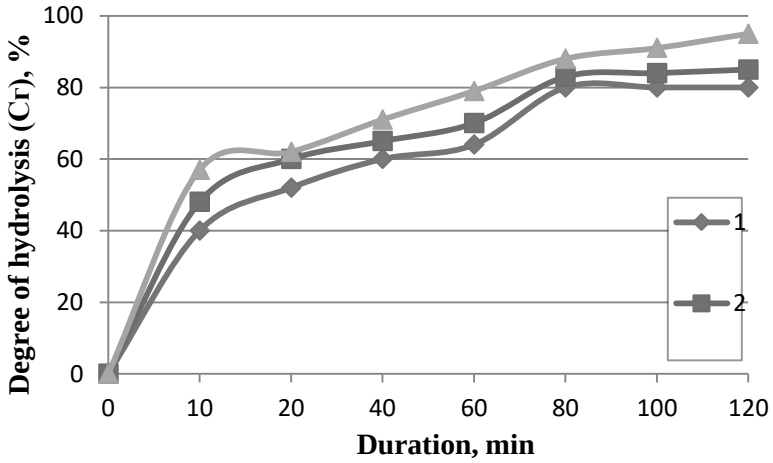

Figure 1.10 - Dependence of the hydrolysis degree of the prepared carrot raw material on the duration of the process of pectin hydrolytic cleavage of : 1 - citric acid; 2 - a mixture of lemon and phosphorus in a ratio of 1: 0.5; 3 - phosphoric acid

Thus, previous studies have shown that the hydrolysis process depends not only on temperature, pH, duration and method of preparation of raw materials, but also on the nature of the hydrolytic factor.

Choice of hydrolytic factor of food quality. Various acids are used to carry out the process of hydrolysis of pectic substances: mineral - hydrochloric, nitric, sulfuric, sulfuric, phosphoric and organic - acetic, citric, oxalic, lactic and others [5].

Hydrochloric acid and most mineral acids are used for hydrolysis of protopectin raw materials, which requires more stringent conditions for this process [2, 40]. Such acids have high chemical activity, so the hydrolysis process is fast compared to acids of organic origin. But mineral acids are aggressive in relation to metals, which causes increased requirements for the choice of materials in the hardware design of the hydrolysis process. In addition, the use of mineral acids determines the need for

neutralization, coagulation of pectin and multi-stage purification [34].

Foreign producers use sulfuric acid or sulfurous gas as a hydrolytic factor, which has lightening properties, is easily removed from the extract by desulfitation and has preservative properties. This acid is chemically weak, which increases the duration of the hydrolysis process from 10 to 24 hours and creates unfavorable working conditions [5, 36].

The use of organic food acids for the hydrolysis process can reduce the duration of the process and the number of technological stages of purification of pectin, as well as to obtain liquid pectin products [36, 51, 57].

The main factors that determine the rate of hydrolysis and yield of pectin - temperature, pH of the medium and duration of the hydrolysis process. For each pectin-containing raw material there are certain optimal values of these parameters.

Studies of the processes of hydrolysis and extraction of pectin substances from pectin-containing raw materials (beet pulp, apple and carrot pomace) were carried out under the following parameters: temperature 70 ... 85 ° C, pH 1.5 ... 2.1 and duration 120 min. Such conditions provided the degree of hydrolysis of protopectin to 92%, the degree of extraction of dissolved pectin from 50% to 80% with an extraction modulus of 1:25 relative to dry matter.

The results of studies of the effect of food acids and their mixtures on the yield of pectin and the degree of esterification are shown in Fig. 1.1, 1.6, 1.7. The research results show that during hydrolysis-extraction the change in the concentration of pectin substances in solution, as well as the change in the degree of esterification of pectin for each type of raw material is different and depends on the type of raw material and hydrolytic factor. The highest yield of pectin for 20 min was observed when using phosphoric acid at a concentration of 1% for all types of raw materials. During the process of hydrolysis-extraction of beet pulp with citric acid, a high yield of pectin was obtained. This is due to the fact that it is a complex and has the appropriate nature of the

reactions to tissues of plant origin. For other types of raw materials (apple and carrot pomace) the best indicators of pectin yield are provided by phosphoric acid. In addition, during the hydrolysis-extraction there is an oscillatory nature of the change in the concentration of pectin in aqueous solution and the degree of its esterification. (Figs. 1.11). The peculiarity of these fluctuating changes in the concentration and degree of esterification of pectin are the characteristic properties of the raw material and its chemical composition. The amplitude of these oscillations is largely influenced by the extractant, and it gives the corresponding values of the minima and maxima of the yield of pectin from raw materials and the corresponding degree of esterification of pectin.

Studies of pectin extraction with food grade acids, taking into account the yield of pectin from raw materials and its degree of esterification, give a general idea of qualitative indicators - the ability to gelation and complexation, as well as physicochemical properties - solubility, viscosity and density [57, 65].

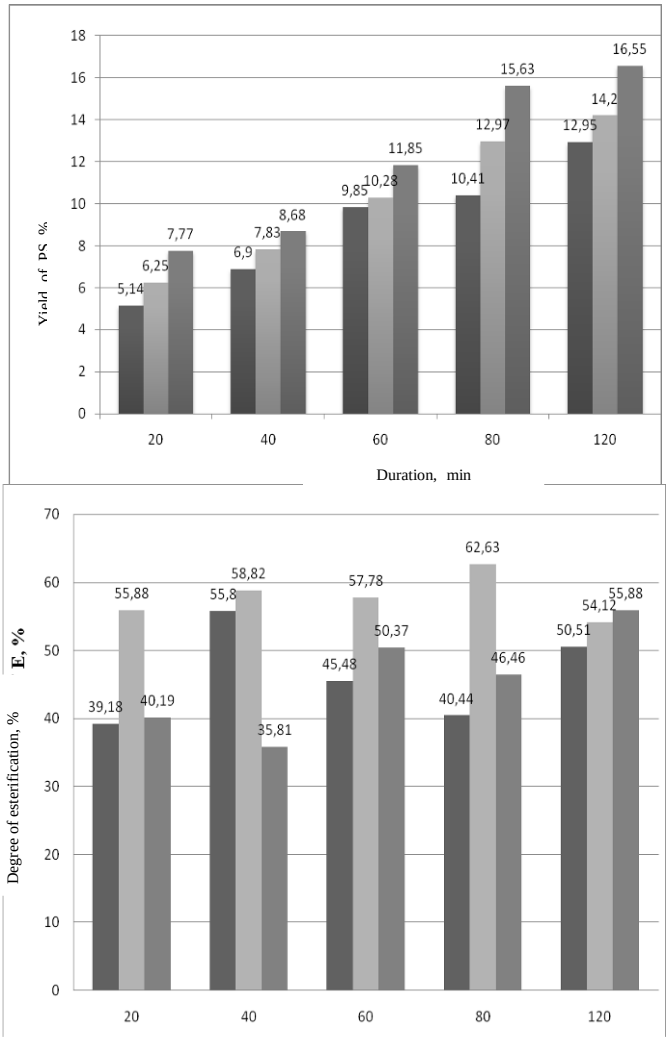

Figure 1.11 - Influence of hydrolytic factors on the yield and degree of esterification of pectin during its hydrolysis-extraction from beet pulp

To determine the optimal conditions for hydrolysis-extraction, experiments were performed to determine the optimization equations and the findings of the extremum functions. Thus, with different parameters of hydrolysis-extraction of different raw materials, the equations of yield Y (%) to dry weight, degree of esterification E (%) and molecular weight (MM) were obtained.:

- beet pulp treated with citric acid with a pH of 2.1

Yield Y, %:

$$Y(\%)=3,06+l,19\text{-}10^{-2}t+5,97\cdot10^{-2}\tau+8,89\cdot10^{-5}t^2-8,17\cdot10^{-5}\tau^2+1,25\cdot10^{-4}t\tau \quad (1.1)$$

where Y_{min} = 5.59 %: Y_{max}= 14.25 %;

Degree of esterification E, %:

$$E\ (\%) = 10,24+0,78\cdot t+0,49\cdot\tau-4,41\cdot10^{-3}\cdot t^2-2,21\cdot10^{-3}\,\tau^2-9,17\cdot10^{-4}\cdot\,\tau\cdot t, \quad (1.2)$$

where E_{min} = 47,6 %; E_{max} = 63,4 %;

Molecular weight MM:

$$MM = 15044,41 + 88,64\cdot t+56,75\cdot\tau-0,41\cdot t^2-0,18\cdot\tau^2-0,23\cdot\tau\cdot t, \quad (1.3)$$

where MM_{min} = 19446; MM_{max} = 21602;

- beet pulps treated with a mixture of citric and phosphoric acids with a pH of 1.8

Yield Y, %:

$$Y\ (\%) = 0,99 + 0,14\cdot t + 3,54\cdot10^{-2}\cdot\tau - 4\cdot10^{-4}\cdot t^2 + 1,94\cdot10^{-5}\cdot t\cdot\,\tau, \quad (1.4)$$

where Y_{min} = 7,75 %; Y_{max} = 16,85 %;

Degree of esterification E, %:

$$E\ (\%) = 4,03 + 0,86t + 0,58\tau - 4,77\text{-}10^{-3}t^2 - 2,09\text{-}10^{-3}\,\tau^2 - 2.22\text{-}10^{-3}t\tau, \quad (1.5)$$

where E = 45,6 %; E_{max} = 62,1 %;

Molecular weight MM:

$$MM = 17640,70 + 53,52t + 24,33\tau - 0,3t^2 - 3,08\text{-}10^{-2}\,\tau^2 - 9,72\text{-}10^{-2}\tau t, \quad (1.6)$$

where MM_{min} = 20011; MM_{max} = 21857;

- beet pulp treated with phosphoric acid with a pH of 1.5

Yield Y, %:

$$Y(\%)=5,6 - 1,83\cdot10^{-2}t+5,06\cdot10^{-2}\tau+6,64\cdot10^{-4}t^2 - 2,14\cdot10^{-5}\tau^2 - 4,11\cdot10^{-5}t\tau, \quad (1.7)$$

where Y_{min} = 7,72 %; Y_{max} = 17,61 %;

Degree of esterification E, %:

$$E(\%) = 12,70+1,08\cdot10^{-2}t + 2,45\cdot10^{-3}\tau - 5,77\cdot10^{-3}t^2 + 2,67\cdot10\tau - 1,49\cdot10^{-3}t\tau, \quad (1.8)$$

where E_{min} = 45,4 %; E_{max} = 59,5 %;

Molecular weight MM:

$$MM = 21827,68 - 39,91t + 63,83\tau + 0,15t^2 - 0,34\tau^2 - 0,25t\tau, \quad (1.9)$$

where MM_{min} = 17398; MM_{max} = 22397;

- apple pomace treated with citric acid with a pH of 2.1

Yield Y, %:

$$Y(\%) = -2,19 + 0,19t + 1,48\cdot10^{-2}\tau - 8,69\cdot10^{-4}t^2 - 2\cdot10^{-5}\tau^2 + 8,44\cdot10^{-5}t\tau, \quad (1.10)$$

where Y_{min} = 5,15 %; Y_{max} = 11,32 %;

Degree of esterification E %:

$$E(\%) = -17,55 + 1,02t + 0,43\tau - 6,07\cdot10^{-3}t^2 - 1,26\cdot10^{-3}\tau^2 - 2,04\cdot10^{-3}t\tau, \quad (1.11)$$

where E_{min} = 60,0 %; E_{max} = 75,4 %;

Molecular weight MM:

$$MM=50909,36 + 58,91t+57,55\tau - 0,35t^2 - 0,21\tau^2 - 6,67\cdot10^{-2}t\tau, \quad (1.12)$$

where MM_{min} = 54309; MM_{max} = 56729;

- apple pomace treated with a mixture of citric and phosphoric acids with a pH of 1.8

Yield Y, %:

$$Y(\%)=-1,71+8,92\cdot10^{-2}t+8,38\cdot10^{-2}\tau - 5,89\cdot10^{-4}t^2 - 4,53\cdot10^{-4}\tau^2 + 5,5\cdot10^{-4}t\tau, \quad (1.13)$$

where Y_{min} = 3,97 %; Y_{max} = 12,19 %;

Degree of esterification E, %:

$$E\ (\%) = 54{,}03 + 0{,}23t + 0{,}19\tau - 1{,}13\cdot10^{-3}t^2 - 5{,}94\cdot10^{-4}\tau^2 - 6{,}33\cdot10^{-3}t\tau, \quad (1.14)$$

where E_{min} = 66,2 %; E_{max} = 72,9 %;

Molecular weight MM:

$$MM = 52243{,}63 + 21{,}10t + 58{,}08\tau - 0{,}12t^2 - 0{,}23\tau^2 - 5{,}14\cdot10^{-2}t\tau, \quad (1.15)$$

where M_{min}= 54430; MM_{max} = 56444;

- apple pomace treated with phosphoric acid with a pH of 1.5

Yield Y, %:

$$Y(\%) = -6{,}15 + 0{,}26t + 1{,}85\ 10^{-2}\tau - 1{,}08\cdot10^{-3}t^2 + 1{,}25\cdot10^{-4}\tau^2 - 1{,}33\cdot10^{-4}t\tau, \quad (1.16)$$

where Y_{min} = 4,00 %; Y_{max} = 12,87 %;

Degree of esterification E, %:

$$E\ (\%) = 45{,}25 + 0{,}62t + 0{,}17\tau - 3{,}49\cdot10^{-3}t^2 - 6{,}94\cdot10^{-4}\tau^2 - 1{,}12\cdot10^{-3}t\tau, \quad (1.17)$$

where E_{min} = 64,2 %; E_{max} = 74,8 %;

Molecular weight MM:

$$MM = 49377{,}37 + 48{,}56t + 95{,}11\tau - 0{,}19t^2 - 0{,}33\ \tau^2 - 0{,}19t\tau, \quad (1.18)$$

where MM_{min} = 53478; MM_{max} = 56916;

- carrot pomace treated with citric acid with a pH of 2.1

Yield Y, %:

$$Y\ (\%) = 4{,}28 + 5{,}45\cdot10^{-2}t - 1{,}91\cdot10^{-2}\tau + 2{,}22\cdot10^{-5}t^2 + 1{,}81\cdot10^{-4}\tau^2 + 2{,}5\cdot10^{-4}t\ \tau, \quad (1.19)$$

where Y_{min} = 6,70 %; Y_{max} = 15,37 %;

Degree of esterification E, %:

$$E\ (\%) = 49{,}46 + 0{,}30t + 0{,}23\ \tau - 1{,}92\cdot10^{-3}t^2 - 1{,}04\cdot10^{-3}\tau^2 + 6{,}83\cdot10^{-5}t\ \tau, \quad (1.20)$$

where E_{min} = 65,0 %; E_{max} = 74,2 %

Molecular weight MM:

$$MM = 14763{,}19 + 43{,}55t + 52{,}07\tau - 0{,}2t^2 - 0{,}17\tau^2 - 0{,}15t\tau, \quad (1.21)$$

where MM_{min} = 17527; MM_{max} = 19373;

- carrot pomace treated with a mixture of citric and phosphoric acids with a pH of 1.8

Yield Y, %:

$$Y(\%) = 6{,}73 - 2{,}8\cdot10^{-3}t - 8{,}6\cdot10^{-3}\tau + 3{,}56\cdot10^{-4}t^2 + 7{,}78\cdot10^{-5}\tau^2 + 3{,}28\cdot10^{-4}t\tau, \quad (1.22)$$

where Y_{min} = 7,55 %; Y_{max} = 15,91 %;

Degree of esterification E, %:

$$E(\%) = 50{,}97 + 0{,}38t - 0{,}35\tau - 2{,}29\cdot10^{-3}t^2 - 1{,}33\cdot10^{-3}\tau^2 - 1{,}88\cdot10^{-3}t\tau, \quad (1.23)$$

where E_{min} = 59,3 %; E_{max} = 77,2 %;

Molecular weight MM:

$$MM = 18316{,}23 + 22{,}64t - 6{,}55\tau - 9{,}65\cdot10^{-2}t^2 + 0{,}12\tau^2 - 7{,}74t\tau, \quad (1.24)$$

where MM_{min} = 18106; MM_{max} = 19468;

- carrot pomace treated with phosphoric acid with a pH of 1.5

Yield Y, %:

$$Y(\%) = -0{,}35 + 0{,}23t - 3{,}3\cdot10^{-2}\tau + 1{,}14\cdot10^{-3}t^2 + 2{,}08\cdot10^{-4}\tau^2 + 3{,}56\cdot10^{-4}t\tau, \quad (1.25)$$

where Y_{min} = 7,82 %; Y_{max} = 16,05 %;

Degree of esterification E, %:

$$E(\%) = 45{,}44 - 4{,}0lt + 6{,}62\tau - 5{,}7\cdot10^{-3}t^2 - 3{,}75\cdot10^{-5}\tau^2 + 5{,}44\cdot10^{-4}t\tau, \quad (1.26)$$

where E_{min} = 55,5 %; E_{max} = 73,6 %

Molecular weight MM:

$$MM = 16354,24 + 21,69t + 30,47\tau - 0,14t^2 - 9,4\cdot10^{-2}\tau^2 - 9,7\cdot10^{-2}t\tau, \quad (1.27)$$

where $MM_{min} = 18029$; $MM_{max} = 19152$.

Based on the results of the study, it was found that the hydrolysis temperature from 70 ° C to 80 ° C increases the yield of pectin, improves its quality and physicochemical parameters (degree of esterification E (%), molecular weight). The results of the analysis show that the optimal temperature of hydrolysis-extraction of pectin substances from beet, apple and carrot raw materials is 80 ° C, duration 90 min.

Determination of protopectin hydrolysis rate constants. The main technological task of the process of chemical destruction of protopectin is to achieve the highest degree of hydrolysis with a minimum duration and depolymerization of pectic substances. One of the limiting factors of the pectin extraction process is the rate of penetration of the hydrolytic factor into the plant tissue by diffusion in the case when the plant tissue was swollen, and by diffusion and sorption in the case when the tissue is partially or completely hydrated. In this case, the partial hydration of dry pectin-containing raw materials penetration of the hydrolytic factor into plant tissue has a sorption nature [40].

Hydrolyzed plant tissue can be considered as a solid with pores filled with pectin solution. The occurrence of a concentration gradient between the solution in the middle of the tissue and outside the tissue leads to the movement of molecules in the direction from the surface of the particle to the liquid phase.

Experimental data on the kinetics of hydrolysis-extraction of pectin-containing raw materials (beet pulp, apple and carrot pomace) with food acids (citric, phosphoric and a mixture of citric and phosphoric) was performed at a pH of 1.5… 2.1, temperature 80 ° C, with hydromodule 1: 25 and duration 120 minutes in order to establish the rate constants of the hydrolytic cleavage reaction of protopectin. The order of the reaction was determined by establishing

the dependence of the logarithm of the concentration on the duration of the reaction, which is described by the equation of the first order. Therefore, the following equation i is used to calculate the rate constants of this process:

$$K_g = \frac{1}{\tau} ln \frac{A}{A-X} \qquad (1.28)$$

where A – the initial amount of the substance (pectin) in the raw material; X – the amount of substance that reacted at a given time; τ – the duration of the hydrolysis reaction.

The results of studies of the hydrolysis rate constants with food acids and their mixture at a temperature of 80 ° C for certain periods of time are given in table. 1.7, where it is shown that the highest reaction rate constant is observed for: beet pulp - phosphorus and lemon; apple pomace - lemon and a mixture of lemon and phosphorus; carrot pomace - phosphorus and a mixture of lemon and phosphorus.

One way to activate molecules is to raise the temperature. It is known that the rate of chemical reactions increases sharply with increasing temperature. According to Van't Hoff's law, when heated by 10 ° C more, the rate constant increases 2 ... 4 times. In the table. 4.7 shows the results of calculating the rate constant of hydrolysis-extraction of pectin substances from beet pulp with a pectin content of 21%, apple pomace with a pectin content of 12% and carrot pomace with a pectin content of 17.36% (to dry weight).

The above data were due to: for heterogeneous reactions, the temperature coefficient is always lower than for homogeneous, because it adds the influence of other factors, and the slowest stage of the process is not the chemical reaction itself, but the process of diffusion, adsorption, etc..

Table 1.7 - **Constants of the rate of protopectin hydrolysis of beet, apple and carrot raw materials at an ambient temperature of 80 °C using different acids**

Duration, min	Hydrolysis constants (K_g, 1/min)		
	Citric acid, pH=2,1	Citric and phosphoric acids,	Phosphoric acid, pH=1,5
Beet pulp			
20	0,012617	0,018066	0,024074
40	0,009522		0,033644
60	0,007596	0,026581	0,01136
80	0,006892		0,025666
120	0,006351	0,050335	
Average value	0,008596		0,025975
Apple pomace			
20	0,024193	0,04177	0,018919
40	0,017329	0,15721	0,014004
60	0,013014	0,014987	0,00898
80	0,027089	0,006021	0,005859
120	0,022567	0,00884	0,029456
Average value	0,020838	0,017468	0,01287
Carrot pomace			
7	0,170467	0,06503	0,118757
20	0,042307	0,035262	0,033517
40	0,022141	0,022998	0,026832
60	0,017238	0,017985	0,028479
80	0,018101	0,025949	0,026014
120	0,01376	0,022915	0,026639
Average value	0,007051	0,03169	0,043373

Accordingly, the rate constant of pectin substances hydrolysis in plant raw materials increases with increasing temperature, but not evenly, although the general trend described by Van't Hoff is maintained.

1.6.2 Physico-chemical properties of pectin extracts

Influence of technological parameters on the degree of pectin esterification in the process of obtaining dry pectin extracts. In the structure of the molecule of all pectins there are carboxyl groups: free -COOH and methoxylated - $COOH_3$. The properties of pectin depend on the ratio of these groups (degree of esterification). Pectins are divided into low-esterified (LEP) and high-esterified (HEP). LEP are used to form complexes with inorganic compounds and are mostly used for therapeutic and prophylactic purposes, and HEP are used in the confectionery industry to form gels. Natural apple pectin belongs to the class of HEP with a degree of methoxylation of 75 ... 78%. The process of demethoxylation, which depends on the influence of pH, temperature and duration of the drying process, was studied on a sample of apple pectin

The study is based on the method of mathematical planning of the experiment. To construct a second-order plan and create a quadratic mathematical model, it was used the optimal matrix of Box (B_p) [41]. This method of planning refers to the D-optimal methods, the use of which allows to obtain the maximum amount of reliable information when conducting the minimum number of experiments. The research was carried out according to the scheme of a three-factor experiment, with the determination of the optimal points of the process.

Factors of influence were selected:

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

t - ambient temperature, °C;

τ - duration, s.

The degree of methoxylation (ξ,%) is considered as a state variable.

Normalization of appropriate factors using dimensionless variables was carried out , the levels of variation of which are given in table. 1.8:

$$XI = (pH - pH_0)/\Delta pH;\ X2 = (t - t_0)/\Delta t;\ X3 = (\tau - \tau_0)/\Delta\tau \qquad (1.29)$$

Table 1.8. - **Levels of factors of plan B_p**

Name	Factors			
	Code	X1	X2	X3
Lower level	-1	2,5	104	5
Top level	+1	3,8	130	18
Zero level	0	3,15	117	11,5
Interval of variation		0,65	13	6,5

After confirming the adequacy of the mathematical model, it was obtained equations for practical calculations:

$$\xi = 931{,}959 - 240{,}721 \cdot pH - 8{,}1904 \cdot t - 2{,}9344 \cdot x + 0{,}222 \cdot pH \cdot t + 0{,}7988 \cdot pH \cdot \tau - 0{,}016 \cdot x \cdot \tau + 33{,}876 \cdot pH^2 + 0{,}0314 \cdot t^2 + 0{,}0548 \cdot \tau^2 \qquad (1.30)$$

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

Viscosity, density, surface tension of concentrated pectin extracts. Viscosity, density, surface tension of highly concentrated pectin extracts were investigated for calculation of technological modes and technological equipment [49, 52-56].

One of the main characteristic properties of pectic substances as lyophilic colloids is viscosity. This is due to the fact that pectin molecules easily associate with each other or with large molecules of concomitant substances, forming aggregates. The second reason is the excessive hydration of polymer molecules, which determines their shape [2].

The viscosity of aqueous pectin solutions and pectin extracts depends on temperature, solids content, pectin content and the nature of pectins (degree of polymerization and esterification, molecular

weight), as well as the content of concomitant substances. Concomitant substances are monosaccharides, proteins, organic acids, salts and others.

The object of the study were highly concentrated pectin extracts from beet pulp, apple and carrot pomace. Pectin extracts were obtained by hydrolysis of protopectin of prepared raw materials with citric acid. The hydrolysis was performed under vacuum for 2 hours at a temperature of 60 ... 80 ° C, pH of the hydrolysis mass 2.5. This technological regime provides the process of extraction of pectin substances with high quality.

After extraction of pectin substances with hot water and purification from insoluble impurities, the extract contained 3 ... 5% of solids and 0.58 ... 2% of pectin.

To obtain pectin extracts in dry form, they must be concentrated to the highest possible content of dry matter and pectin. When the concentration of pectin extract is more than 18% of solids and 10% of pectin substances, it becomes non-technological in production, as a result of increasing its viscosity. In addition, when concentrated in a vacuum evaporator under the action of temperature and air, colored substances are formed due to the reaction of melanoidin formation and oxidation of phenolic compounds. Rotary film evaporators or membrane filters are used in the production to concentrate solutions. In this case, pectin-containing solutions or extracts are exposed to less temperature and the duration of their concentration is reduced.

Laboratory vacuum rotary evaporator IR-10 was used to concentrate pectin extracts. Concentration took place for 4 ... 6 h at a temperature of 60 ... 70 ° C. Under such conditions, all the initial properties of pectin are preserved.

During the concentration of pectin extracts samples were taken with different concentrations of dry and pectin substances (PS). At a temperature of 20 ° C, the density and dynamic viscosity of the extracts were determined.

Dynamic viscosity studies were performed using a Hepler viscometer [25].

The study of the dependence of the density (p) and dynamic viscosity (μ) of pectin extracts on the mass fraction of pectin at a temperature of 20 ° C is given in table. 1.9.

Table 1.9 - **Density and dynamic viscosity of pectin extracts depending on the mass fraction of pectin**

Beet pectin extract						
Solids, %	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						
Solids, %	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	8,36
Carrot pectin extract						
Solids, %	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

The change of these parameters depending on temperature was investigated. The temperature range was chosen from 20 ° C to 80 ° C, with a measurement interval of 10 ° C, the research results are given in table. 1.10.

Table 1.10 - **Density and dynamic viscosity of pectin extracts depending on temperature**

Parameters	**Temperature, t °C**						
	20	**30**	**40**	**50**	**60**	**70**	**80**
Beet pectin extract Solids =18 %, PS =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 Solids =18 %, PS =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 Solids =18 %, PS =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

In addition to the results of the density and dynamic viscosity of pectin extracts, it is necessary to know the values of the surface tension of these solutions, for calculations of spraying and drying parameters. Depending on the value of surface tension, it can be determined the initial diameter of the drop when spraying, etc. [42, 54, 63, 64]. In the table 1.11 shows the value of surface tension of pectin extracts at the maximum concentration of dry and pectin substances depending on temperature.

The surface tension of the liquid is determined by the nature of the substances in solution. Some of them, related to surfactants are able to reduce surface tension. One such surfactant is pectin, which exhibits emulsifying and foaming properties [5].

Table 1.11 - **Surface tension of pectin extracts**

Parameters	**Temperature, t °C**						
	20	**30**	**40**	**50**	**60**	**70**	**80**
Beet pectin extract Solids =18 %, PS =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 Solids =18 %, PS =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
Apple pectin extract Solids =18 %, PS =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 Solids =18 %, PS =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

Analysis of the obtained experimental values of the characteristics of pectin extracts makes it possible to establish patterns of changes in density and dynamic viscosity depending on the concentration of dry and pectin substances, and changes in density, dynamic viscosity and surface tension depending on temperature at constant concentrations of dry and pectin substances [60].

1.6.3 *Complexing ability of extracts*

The ability to complexation of pectin substances depends on the content of free carboxyl groups, ie the degree of esterification of carboxyl groups with methanol. The degree of esterification determines the linear charge density of macromolecules, as well as the strength and method of cation binding. This ability depends on the structure and degree of pectin purity, the nature of metals that interact with pectins, the pH of the medium in which complexation takes place and other factors [65-67].

Liquid, concentrated, dry pectin extracts and pectins obtained from beet, apple and carrot raw materials were selected for the study of the ability to complexation.

Studies to determine the ability to complexation of beet, apple and carrot pectin extracts with a pectin content of 5 g per 100 g of extract within the pH of 1.5 ... 8 (Fig.1.12).

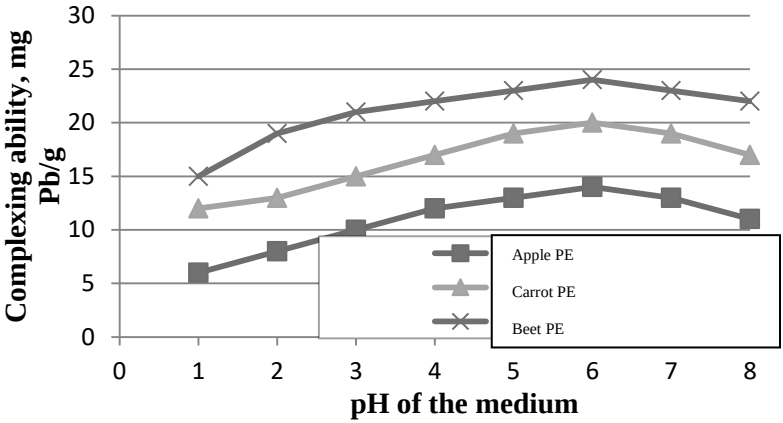

Figure 1.12 - Dependence of the complexing ability of pectin extracts on the pH of the medium

The results of research show that the greatest ability to complexation of pectin extracts is observed at pH 6.0 ... 7.5 and is for beet - 24.2, apple - 13.8 and carrot - 19.6 (mg Pb^{2+}/g).

The ability to complexation of pectin extracts depending on the pectin content was investigated (Table 1.12).

The study of the ability to complexation of pectin extracts showed that it increases in proportion to the increase in pectin content in the extract and reaches the highest value for dry beet pectin extract (180 mg Pb^{2+}/g).

Table 1.12 - **The ability to complexation of pectin extracts, mg Pb^{2+}/g**

The name of the extract	Pectin content in the extract, %		
	1	5	35
Beet	4,4	25	180
Apple	1,9	10,8	105
Carrot	3,6	21,5	150

The values of the ability to complexation of pectin extracts were compared with pectin, which was isolated from the obtained dry extracts, and which were, respectively: for beet - 375 mg Pb^{2+}/g, apple pectin - 260 mg Pb^{2+}/g, carrot - 345 mg Pb^{2+}/g. High values of the ability to complexation of pectins due to the fact that in the drying process reduces the degree of esterification and increases the content of carboxyl groups.

1.6.4 *Gelling ability of pectin extracts*

The ability of pectins to gelation, which are obtained by changing certain parameters of technological processes, is one of the criteria for assessing the effectiveness of technological processes of production of pectin and pectin products. The study was performed with pectin extracts obtained from apple, carrot pomace and beet pulp using as a hydrolytic factor - citric acid.

In the technology of jelly products with pectin acid (citric, lactic) provide buffering system pectin-sugar-acid, as well as inhibits the dissociation of polygalacturonic acid, which is one of the factors in the formation of pectin gel [57]. That is, the presence of citrate ions in pectin extracts eliminates the additional introduction of food acids. The main indicators of pectin, which determine the type of gelation and its ability to form gels, are the molecular weight and the degree of esterification. Highly esterified pectins (E = 68 ... 78%) form gels in the presence of 60 ... 65% sugar and 1% acid, low esterified pectins (E = 35 ... 50%) can form gels at much lower sugar concentrations or at all without it in the presence of polyvalent metal ions [2]. Therefore, we studied samples of pectin extracts, pectin which has the following indicators:

- liquid apple extract, pectin content 4%, degree of esterification 72%, molecular weight - 250000;
- dry apple extract, pectin content 40%, degree of esterification 45%, molecular weight - 180000;

- liquid carrot extract, pectin content 4%, degree of esterification 48%, molecular weight - 23000;

- liquid beet extract, pectin content 4%, degree of esterification 42%, molecular weight - 22000.

The ability to gelation liquid apple pectin extract was determined in the system of pectin-sugar-acid, dry apple, carrot and beet - in the system of pectin-ion Ca-sugar (Fig. 1.13). Calcium chloride at the rate of 40 mg of salt per 1 g of pectin was used as a source of calcium ions.

Apple extracts have the highest ability to form gels (48 ... 56 kPa), which allows them to be used as gelling agents in the production of jelly confectionery, beets and carrots have the lowest ability. Such extracts can be used as thickeners, stabilizers in the production of canned goods, dairy products and the like.

The ability to geletion varies for each type of pectin in a certain range of pH values. Therefore, studies of the effect of pH on the ability of pectin extracts to gelation (Fig. 1.13).

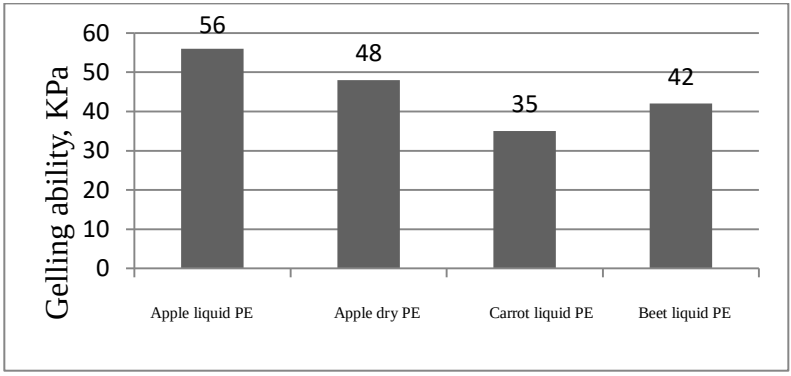

Figure 1.13 - Ability to gelation of pectin extracts

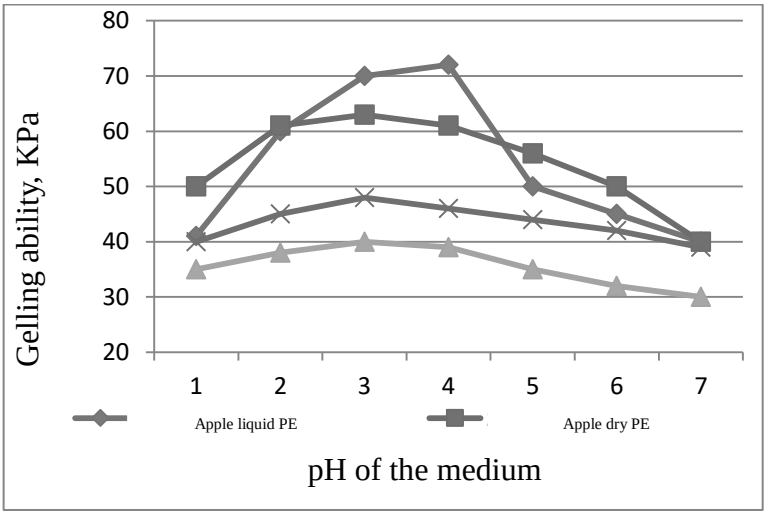

Figure 1.14 - Dependence of the ability to gelation of pectin extracts on the reaction medium

The results of research show that the maximum ability to gelation has a liquid apple pectin extract in the range of pH = 2.8 ... 3.6. For low-esterified extracts (apple, carrot, beet) the region of maximum gelation is much wider and the reaction medium is pH = 2.5 ... 4.8.

In the study of the ability to gelation of dry beet and carrot pectin extracts, it was found that they do not form strong gel structures. This is due to the fact that pectic substances in the drying process undergo certain changes, namely the degree of esterification (E = 28 ... 30%) and molecular weight (10000 ... 16000). Such pectin extracts can be used as stabilizers in nutrient media, or as biologically active additives in products for therapeutic and prophylactic purposes.

1.6.5 *Technological scheme of dry pectin extracts production*

Based on the results of laboratory research and analytical calculations, a technological scheme was developed and equipment for obtaining dry pectin extracts was selected [45-48, 50].

A distinctive feature of the technology is its zero-waste, versatility, safety and environmental friendliness. Selection of equipment, pipelines and implementation of technological regimes were carried out depending on the physicochemical parameters of pectin (active interaction with metal ions, resistance to high temperatures, adsorption properties, viscosity), as well as changes in pH from 1.5 to 3.5.

In fig. 1.15. the technological scheme of production of dry pectin extracts is presented.

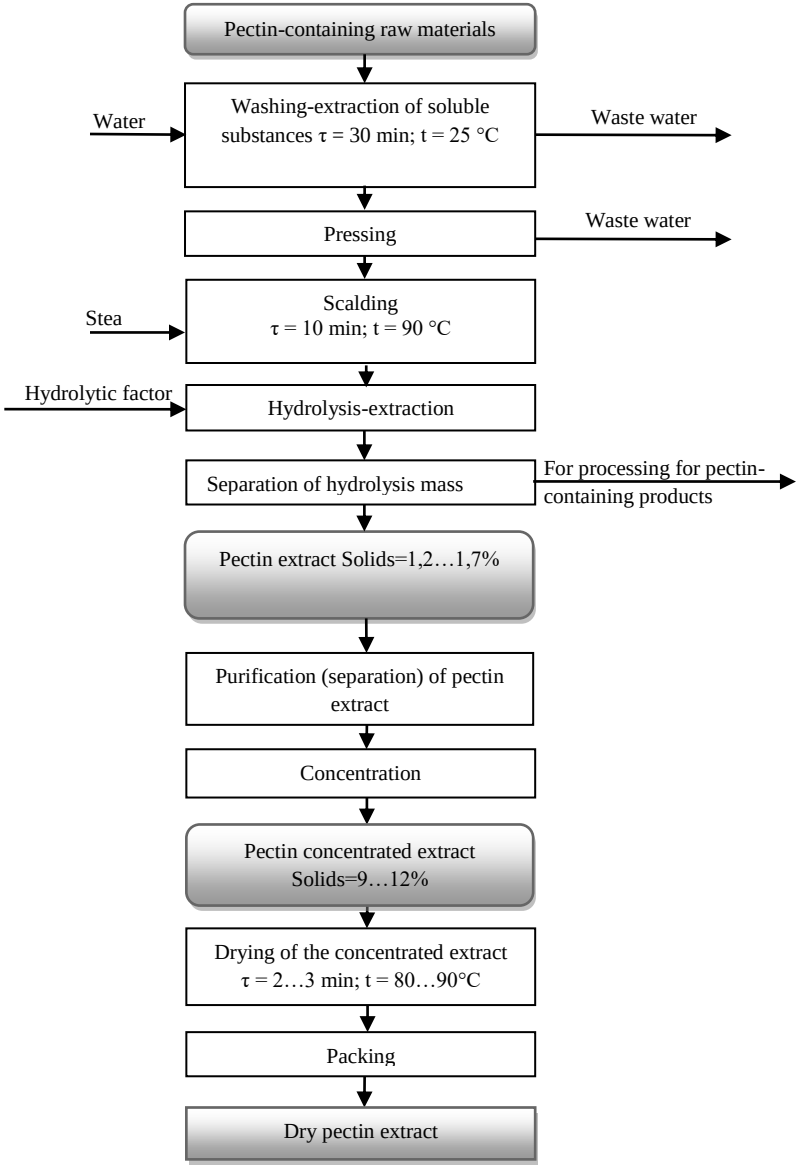

Figure 1.15 - Technological scheme of production of dry pectin extracts

Pre-prepared pectin-containing raw material enters the extractor, where it is mixed with drinking water in a ratio of 1: 3 at a temperature of 40 ... 50 ° C for 15 ... 20 minutes. For better removal of soluble ballast substances relative to pectin, the raw material is separated from free water on a separating sieve, then pressed to a humidity of 88 ... 90%, then blanched at a temperature of 90 ... 95 ° C for 5 ... 7 minutes and sent for hydrolysis-extraction. Hydrolysis-extraction takes place in devices of periodic action under a vacuum of 0.075 MPa for 120 minutes. The hydrolytic factor is prepared in a separate device and sent to the hydrolyzer. After hydrolysis of the protopectin, the hydrolysis mass is pumped to the drain, where the separation of the free extract from the hydrolysis mixture. The separated extract is purified by separation and concentrated and dried in a spray dryer, then packaged in plastic bags of 25 kg.

If necessary, pectin extract is neutralized to pH = 3..3,5, which in turn softens the conditions of concentration and drying [58].

Apparatus-technological scheme of production of dry pectin extract is presented in fig. 1.16.

Freshly squeezed raw materials or recovered dried, fed to the extractor 1, where it is mixed with water and further washed. From the extractor 1 the raw material is pumped by pump 2 to the separating sieve 3, which separates the mixture from the washing water. After the separating sieve 3, the mixture passes into the screw press 4, where it is pressed to a moisture content of 88 ... 90%, and the outflow is disposed of. From the auger press, the raw material is transferred to the scraper 5, where it is blanched at a temperature of 80 ... 90 ° C for 5 ... 7 minutes.

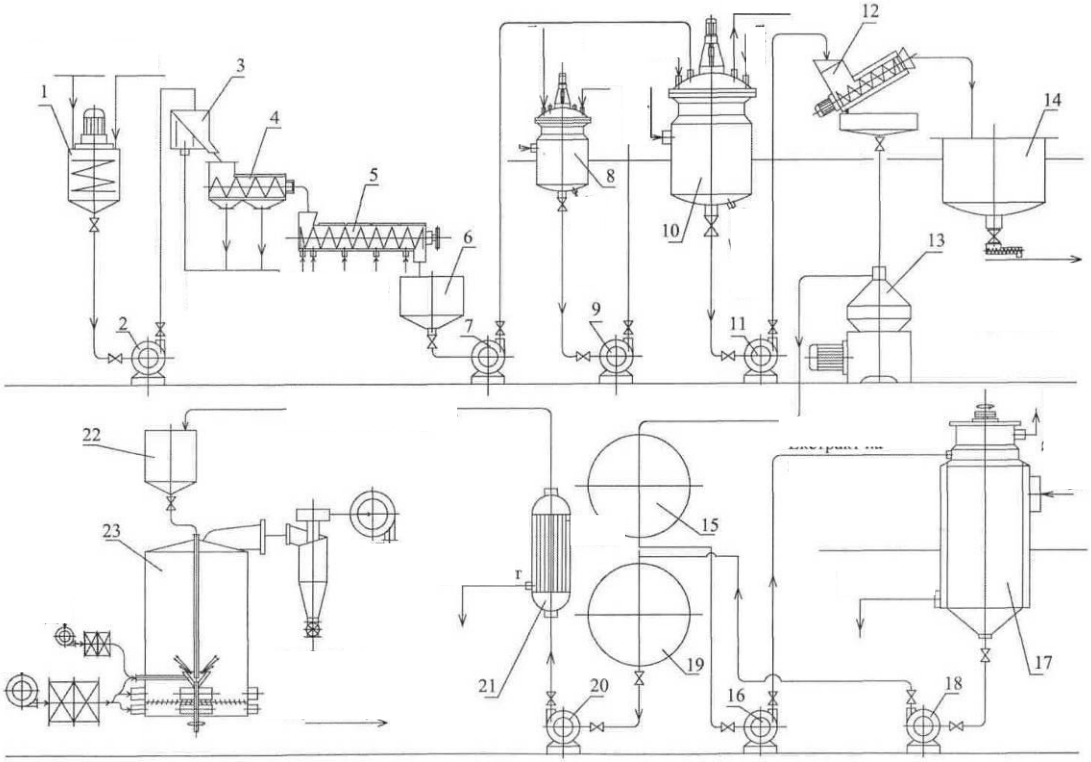

Figure 1.16 - Apparatus-technological scheme of processing of secondary apple raw materials to obtain pectin products: 1-2 - scraper conveyor; 3-4 - extractors; 5 - screw press, 6 - noria; 7 - belt conveyor; 8 - pumps; 9 - capacity for diffusion juice; 10 - capacity; 11 - collector-heater extractant; 12 - hydrolyzate; 13 - separating sieves; 14 - drain; 15 - collection; 16 - pressure head collection; 17 - filter; 18 - cooling bath; 19 - separator; 20 – filter press.

Blanched raw materials are fed to the collector 6, and then the pump 7 is pumped into the hydrolyzer 10, in which the tank 8 is prepared prepared extractant pump 9. After hydrolysis of raw materials, the mixture from the hydrolyzer is pumped by the pump 11 to the drain 12, where the separation of liquid and solid phase. The humidity of the solid phase is 97%. The separated extract is purified on a separator 13 and fed to the collection of purified extract 15, and the remaining hydrolyzed mass from the drain 12 is fed to the collection 14, where it is sent for processing for pectin-containing products. The purified extract from the collection 15, the pump 16 is fed to the vacuum evaporator 17. In the vacuum evaporator, the extract is concentrated to a dry matter content of 18% and fed by the pump 18 to the collection of concentrated extract 19. From the collection of concentrated extract 19 by pump 20 through the heat exchanger 21 is fed to the collector 22 and then sent for drying in a spray dryer 23, where the dry pectin extract is fed for packaging.

1.7 Pectin-containing purees and their functional and technological properties

From the literature it is known that vegetable raw materials contain a unique chemical composition (table.1.15) [68].

Table 1.15 - **Chemical composition of carrot and pumpkin purees**

Chemical composition	The amount of 100 g of product	
	Carrot puree	Pumpkin puree
Water, g	88.0	90,0
Proteins, g	1.3	1.0
Carbohydrates, g Mono- and disaccharides, g Starch, g	6.9 6.7 0.2	4.4 4.2 0.2
Dietary fiber, g	2.4	2.0
Organic acids, g	0.3-0.8	2.0
Pectic substances, g	0.9	0.4
Ash	0.54-1.7	0.6
Vitamins		
Beta-carotene, mcg	5,1	4.8
Vitamin B1 (thiamine), mg	0.06	0.05
Vitamin B2 (riboflavin), mg	0.07	0.06
Vitamin B3 (Niacin), mg	0.3	0.4
Vitamin B6 (Pyridoxine), mg	0.1	0.1
Vitamin B9 (folic acid), mcg	9.0	14.0
Vitamin C, mg	5.0	8.0
Vitamin E, mg	0.6	
Vitamin PP, mg	1.0	0.5
Macronutrients		
Calcium, mg	27.0	25.0
Potassium, mg	200.0	204.0
Magnesium, mg	38.0	14.0
Sodium, mg	21.0	4.0
Phosphorus, mg	55.0	25.0
Sulfur, mg	6.0	18.0
Trace elements		
Iron, mg	0.7	0.4
Zinc, mcg	400.0	240.0
Iodine, mcg	5.0	1.0
Bor, mkg	200.0	
Copper, mcg	80.0	180.0
Cobalt, mcg	2.0	1.0
Manganese, mcg	200.0	40.0
Fluorine, mcg	55.0	86.0

Carrot puree is a source of carbohydrates, biologically active substances and mineral compounds. Carbohydrates are mainly fiber, pectin, hemicellulose, sucrose, glucose and fructose. 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. Carrot puree contains phospholipids, lecithin and sterols. Inositol, which is found in the pulp, mainly acts as a prophylactic and therapeutic agent for atherosclerosis, as it has the ability to improve lipid metabolism in the body. Among the minerals are potassium, phosphorus, chlorine and magnesium. In terms of magnesium, carrot raw materials surpass all other vegetable raw materials. It affects vascular expansion, activates intestinal motility. Carrot puree has numerous trace elements - aluminum, boron, vanadium, iron, iodine, cobalt, copper, manganese, zinc. Therefore, carrot products are recommended for patients with hypothyroidism.

Pumpkin is a valuable vegetable raw material. It is known that pumpkin has a positive effect on diseases of the liver, kidneys, gastrointestinal tract, cardiovascular system, improves digestion. Pumpkin puree contains fiber, pectin, sugary compounds (glucose, fructose, sucrose), organic acids (mainly malic). Vitamin composition is represented by vitamins C, B_1, B_2, D, carotene. Pumpkin raw materials - 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, it regulates digestion and due to its high content of pectin, promotes the excretion of cholesterol. Pumpkin products are recommended to include in the diet of patients with hepatitis and cholecystitis, people with gallstones, chronic colitis and enterocolitis, with diseases of the cardiovascular system (hypertension, atherosclerosis with circulatory failure), with acute nephritis and pyelonephritis.

Vitamin composition is represented by β-carotene, vitamins C, B_1, B_2, folic acid. Pumpkin and carrot puree contain a large amount of minerals: especially potassium (more than 200 mcg per 100 g / product), calcium, phosphorus, magnesium. Trace elements are iron, zinc, aluminum, boron, vanadium, iodine, fluorine, manganese, molybdenum.

In the production of fruit fillings and jelly semi-finished products, apple puree is mainly used, which has a high content of pectin (1.0… 1.2 g per 100 g of product). But carrot and pumpkin puree also contains a significant amount of pectin, in addition to high content of dietary fiber - fiber and hemicellulose.

In order to increase the amount of water-soluble pectin in vegetable raw materials it was proposed a new method of preparation of vegetable, fruit and fruit-vegetable purees, which is protected by the patent of Ukraine [69]. The peculiarity of their production is the process of acid hydrolysis of vegetable raw materials in order to enrich the puree with water-soluble pectin due to the partial destruction of protopectin, which is contained in the cell membranes and intercellular walls of vegetables. In order to preserve the biologically active substances of vegetable puree, the process of hydrolysis of protopectin is carried out in a mild mode: with citric acid at a temperature of 68… 70 ° C, pH - 3.0… 3.2, for 40… 45 minutes. However, hydrolytic cleavage should not only transfer the protopectin of vegetable raw materials into water-soluble pectin, but also certain changes in its qualitative and quantitative composition. Therefore, the first stage of research was to establish the main components and characteristics of hydrolyzed vegetable raw materials.

The object of the study was selected carrot and carrot hydrolyzed puree from carrots "Shantane", pumpkin puree from pumpkin "Gilea". Comparative characteristics of changes in the chemical composition of vegetable and apple purees in the hydrolysis process are given in table. 1.16.

It should be noted that in the process of hydrolysis of carrot, pumpkin and apple puree, the active acidity decreased to pH 3.2.

Due to the hydrolysis of protopectin of plant tissues, the amount of water-soluble pectin in apple hydrolyzed puree (AHP) increased in 1.6 times, in carrot hydrolyzed puree (CHP) in 2 times, in pumpkin hydrolyzed puree (PHP) almost 3 times. This can be explained by the different structure of the molecule of protopectin apple, carrot and pumpkin purees. The fiber content decreased, but slightly - by 0.5… 1.0%. This is probably due to the partial hydrolysis of insoluble protopectin fibers.

The amount of vitamin C decreased by 30… 35%, which is probably due to partial thermal destruction during acid hydrolysis..

Table 1.16 - **Comparative characteristics of the chemical composition of non-hydrolyzed and hydrolyzed apple, carrot and pumpkin purees**

Indicator	Apple puree		Carrot puree		Pumpkin puree	
	AP	AHP	CP	CHP	PP	PHP
Solids, %	10,0±0,2	10,0±0,2	11,0±0,2	11,0±0,2	11,0±0,2	11,0±0,2
Active acidity, pH	4,0±0,1	3,2±0,1	5,7±0,1	3,2±0,1	5,8±0,1	3,2±0,1
Water-soluble pectin content, g/100 g of product	1,2±0,1	2,0±0,1	0,7±0,1	1,4±0,1	0,6±0,1	1,8±0,1
The degree of esterification of pectin, %	70±2	70±2	40±2	40±2	60±2	60±2
Aiber content, to the amount of solids,%	32,8±0,5	32,3±0,5	35,4±0,5	34,2±0,5	37,5±0,5	35,8±0,5
The content of reducing substances, %	0,03±0,1	0,2±0,1	0,8±0,1	1,3±0,1	1,2±0,1	2,0±0,1
Vitamin C content,	7,5±0,	5,3±0,	4,8±0,	3,4±0,	6,4±0,	4,6±0,

mg/100 g of product	3	3	3	3	3	3
Content of β - carotene, mg /100 g of product	0,9±0,3	0,8±0,3	5,85±0,3	5,3±0,3	3,85±0,3	3,5±0,3

One of the important biologically active components present in carrot puree (CP) and pumpkin puree (PP) is β - carotene. Under the action of the enzyme carotenase β - carotene is broken down into 2 molecules of vitamin A. In addition, ß-carotene is a natural dye that gives a bright orange color. It was found that in the process of hydrolysis of CP and PP the amount of β - carotene decreased, but slightly - by 0.3… 0.5%.

It is known that fiber, pectin, β - carotene have a pronounced therapeutic and health effect and transfer it to food obtained with their use. Thus, plant fiber is characterized by the ability to bind insoluble complexes and excrete radionuclides, heavy metals, nitrates and other toxic compounds. Enrichment of traditional foods with pectin, promotes the excretion of heavy metals. Thus, the use of vegetable purees will contribute to the enrichment of food products with biologically active substances and increase the nutritional value.

A review of the literature did not reveal information on the degree of esterification of pectin in carrot and pumpkin purees. According to the results of research it was found that the degree of esterification of pectin in non-hydrolyzed and hydrolyzed puree is: carrot - 38… 40%, pumpkin - 58… 60%, apple - 70… 72%. That is, the process of mild hydrolysis of protopectin has almost no effect on the degree of esterification.

Thus, apple puree (AP) contains HEP with a large number of methoxyl groups and belongs to the pectins with a high rate of gelation (high gardening); pumpkin puree also contains HEP, but less methoxyl groups and it belongs to the pectins of the slow garden; carrot puree contains LEP.

Given that the mechanisms of jelly formation of HEP and LEP of pectins differ significantly, it is possible to envisage a different mechanism of formation of jelly-like structure of semi-

finished products based on carrot, pumpkin, apple purees and their blends.

The mechanism of jelly formation for HEP pectins is sugar-acid. That is, the formation of a jelly-like structure based on pumpkin and apple purees requires the presence of sugar and low pH (3.2 - 3.5).

LEP form jellies according to the model of "egg" package in the presence of calcium ions. That is, in the formation of a jelly-like structure based on carrot puree, it is necessary to add calcium salts - calcium chloride or citrate. In this case, sugar and acid are not particularly important for the solidification of the jelly- when using LEP, the grid structure of the jelly is formed due to calcium pectinates. Thus, the use of CHP will promote the creation of jelly structures with low sugar content and, accordingly, reduce the caloric content of products. In addition, analysis of the chemical composition of carrot puree showed the presence of calcium ions - up to 50 mg per 100 g of product. This should affect the formation of the jelly-like structure.

Based on the research, it was concluded that when creating a new range of semi-finished products with a gelatinous structure based on CHP, CAHP, PHP must take into account the peculiarities of their chemical composition and physicochemical properties.

The process of structure formation of gelatinous semi-finished products based on vegetables depends on many technological factors, one of which is the degree of hydrophilicity or the degree of swelling. When swollen, a low molecular weight compound is absorbed by a high molecular weight compound (HMWC), resulting in an increase in the volume and mass of the high molecular weight compound. In general, swelling is considered as the first stage of the dissolution process. Macromolecules in amorphous macromolecular substances are relatively loosely packed, so gaps are formed between flexible chains, into which water molecules diffuse. There is hydration of macromolecules, which is accompanied by the destruction of the bonds between individual macromolecules and the location of water molecules near the

macromolecules. This initial hydration weakens the bonds in the links and promotes the penetration of water molecules into the HMWC. This process goes through a transitional stage of swelling, when the particles swell and increase in size due to the forces of cohesion between macromolecules.

In hydrolyzed purees of carrot, pumpkin and apple, hydrophilic compounds are represented by pectin and fiber. But the degree of their swelling will depend on the linear size of macromolecules, structural features, the content of different functional groups. Due to the fact that CHP, PHP and AHP contain pectin with different degrees of esterification and different amounts of fiber, studies have been conducted to determine the degree of swelling of polysaccharides of dried plates of non-hydrolyzed and hydrolyzed puree. Curves of kinetics of swelling of puree are shown in fig.1.17.

For all samples, the degree of swelling of polysaccharides of hydrolyzed puree was higher than usual. This phenomenon can be explained by the fact that in the process of hydrolysis significantly increases the amount of water-soluble pectin, which has high moisture-absorbing properties.

According to research, it has been found that pumpkin puree polysaccharides have the best ability to swell. The degree of swelling of polysaccharides PP is 1.2%, PGP - 1.3%. This is due to the higher content of pectin - 0.6% in PP and 1.8% in PPP.

The degree of swelling of polysaccharides CP is 0.82%, CHP - 0.98%. The lowest degree of swelling was observed in polysaccharides of apple puree: AP - 0.48%, AGP - 0.58%, almost in 2.2 times lower than polysaccharides of pumpkin puree and 1.7 times polysaccharides of carrot puree.

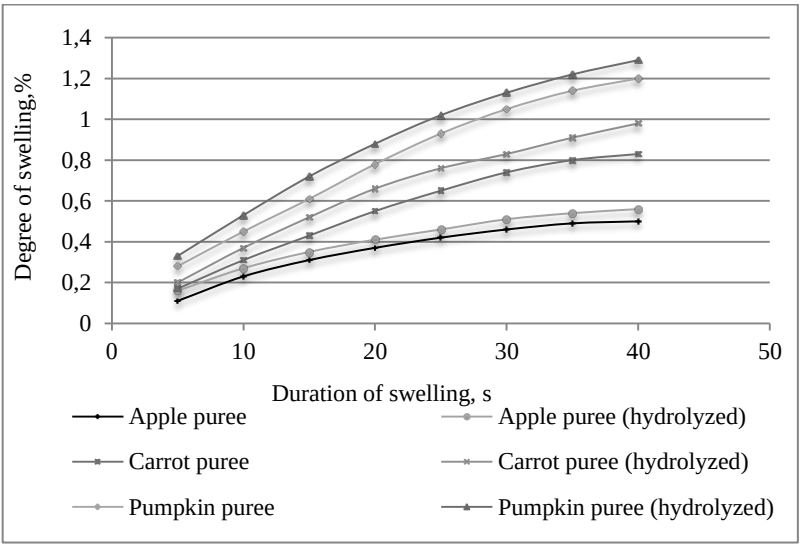

Figure 1.17 - Dependence of the degree of polysaccharides swelling of non-hydrolyzed and hydrolyzed pectin-containing purees on the duration of the process

It should be noted that in the analysis of the microstructures of PHP and CHP, it was determined that the particle size of fiber in CHP is 20 μm, PHP - 8 μm, it also helps to increase the degree of swelling of PHP.

According to the results of research, it is proved that the degree of swelling depends on the duration of hydration, while for 40 s it was increased by 4.3 times for PHP, 4.9 times for CHP, and 3.6 times for AHP.

Studies of the rheological properties of carrot, pumpkin and apple hydrolyzed purees were performed on a rotary viscometer "Peotest-2" at a temperature of 25ºC. It was found that the obtained systems are structured and exhibit pseudoplastic properties. All studied systems have a developed supramolecular structure of the coagulation type, which with increasing load (stress in the system) collapses and viscosity decreases (Table 1.17). In this case, the

viscosity drops to the lowest value of η_m, which corresponds to the practically destroyed supramolecular structure.

Table 1.17 - **Rheological characteristics of carrot, pumpkin and apple hydrolyzed purees (n=3, p<0,05)**

№	System	η, Pa·s			P, Pa			P_{k1}/P_{k2}	P_m/P_{k1}
		η_0	η_m	$\eta_0-\eta_m$	P_{k1}	P_{k2}	P_m		
1	PHP	149,3	1,5	147,8	592,0	1005,1	1400	0,6	2,4
2	CHP	126,5	1,4	125,1	637,6	1235,5	1504,8	0,52	2,36
3	AHP	50,6	1,3	49,3	227,7	910,8	1200	0,25	5,2

All systems are structured, but in systems without added sugar there is an avalanche of destruction of the structure. The most prone to destruction system - AHP. PGP and CHP systems are approximately equally prone to failure and can withstand voltages of 500 - 3000 Pa. The research results are shown in Fig. 1.18.

It was found that with increasing acidity within the established limits, the content of protopectin decreases from 21.17% (of the total dry matter of apple) to 15.03%, and soluble pectin, respectively, increases from 4.50% to 10.5% on the background relative to the constant amount of pectin (average 25.62%). This can be explained by the softening of apple tissues during heat treatment with a significant decrease in the values of active acidity, which, in turn, contributes to a greater degree of destruction of protopectin.

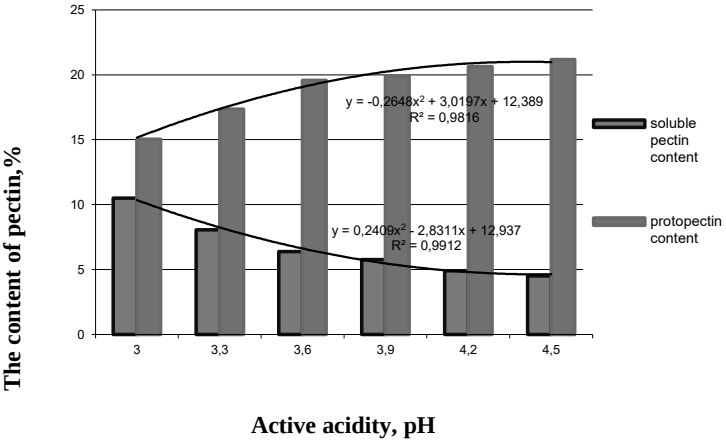

Figure 1.18 - The effect of active acidity on the ratio of pectin in apple puree

The graph clearly shows that at pH 4.2… 4.5 the smallest transition of pectin to soluble form is observed, and at pH 3.0… 3.3 this content is the maximum, which is generally consistent with existing data of other scientists on the conditions destruction of protopectin in pectin-containing raw materials of a number of fruits and vegetables.

The established effect will help to increase the functional and technological properties of apple puree as a stabilizing agent.

The change in the degree of esterification of pectin substances depending on the active acidity is given in table.1.18.

Water-soluble pectin derived from protopectin (PP) - the insoluble fraction of pectin in apples - can be attributed to highly esterified pectins, as the value of the degree of esterification for soluble pectin (SP) in the studied samples ranges from 59.96 to 70.36%.

Table 1.18 - **The degree of esterification of pectic substances in apple puree at different values of active acidity (n=5, P=0,95)**

The value of active acidity, pH					
3,0		3,3		3,6	
SP,%	PP,%	SP,%	PP,%	SP,%	PP,%
70,36±1,37	76,54±1,60	65,38±0,94	79,95±1,35	61,16±0,97	64,04±1,15
3,9		4,2		4,5	
SP,%	PP,%	SP,%	PP,%	SP,%	PP,%
61,92±1,01	51,52±1,20	59,96±0,87	49,65±0,86	60,08±1,20	49,40±1,09

For protopectin, the maximum value of the degree of esterification is slightly higher and reaches 79.95%. Slight fluctuations in the degree of esterification for SP are observed only within the active acidity pH 3.0… 3.3, which corresponds to a well-known pattern for PP. This suggests that during the acid-heat treatment a significant amount of pectin is released with high quality (high degree of esterification, high molecular weight). Thus, for the maximum activation of pectic substances of apple puree, it can be recommend a range of active acidity values of 3.0… 3.3.

Apples are a very promising raw material in food production not only in chemical composition, physical and technological properties, nutritional and biological value, but also in the ability to bind moisture [8]. To compare the effect of heat treatment and active acidity on the moisture binding capacity of apple puree, apple pulp without heat treatment was selected for control samples (sample №1). In samples № 2-5 the active acidity was from 3.9 to 3.0 units of pH. The obtained data are given in table. 1.19.

Table 1.19 - **Moisture-binding capacity of apple puree at variable active acidity**

Sample number	Active acidity of samples, units pH	Humidity, %	Water content, %		Moisture content, g/g dry matter	Bound water content. g/g dry matter
			Free	Bound		
1	4,2	84,81 ±1,52	81,08 ±2,01	18,92 ±0,44	5,58±0,13	1,056±0,025
2	3,9	85,54 ±1,72	80,07 ±1,49	19,93 ±0,42	5,92±0,12	1,179±0,022
3	3,6	86,06 ±1,38	80,86 ±1,70	19,14 ±0,38	6,18±0,14	1,182±0,029
4	3,3	86,10 ±1,98	80,40 ±1,21	19,60 ±0,46	6,19±0,15	1,214±0,018
5	3,0	86,42 ±1,61	78,90 ±1,46	21,10 ±0,33	6,36±0,12	1,342±0,032

The results of research suggest that heat treatment and changes in active acidity to values of 3.0-3.3 have a significant impact on the ability of apple puree to bind moisture.

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2 DEVELOPMENT OF BEET PECTIN TECHNOLOGY FROM BIOCHEMICALLY TREATED RAW MATERIALS

2.1 Analysis of beet pectin technologies

Modern industrial technology for the production of pectin is based on acid-thermal hydrolysis of raw materials and consists of four main groups of processes [1].

The first of them includes the preparation of raw materials, hydrolysis-extraction of pectin, purification and concentration of pectin extract. The second group includes processes for the extraction of pectin from the liquid phase as a dry product and its standardization. Foreign production schemes involve the production of pectin with different properties, which determines the third group of processes: additional purification of pectin extract and coagulate at different technological parameters to achieve the specified rates of gelation and the ability to complexation[2]. The fourth group combines the processes of regeneration of aliphatic alcohols used in the processes of the second group, and the disposal of solid residues and effluents of pectin production.

In world practice, for the production of commercial pectin are used mainly apple pomace and citrus peels.

Beet raw materials (sugar and fodder beet, beet pulp) meets all the requirements for its use in the industrial production of pectin. A feature of beet raw materials is the content of protopectin in the amount of 95-98% of the total amount of pectin, which determines the parameters of the extraction of the target product [1].

Preparation and canning of beet pulp for pectin production. Particular attention in the production of pectin is paid to the quality of pectin-containing raw materials. The main requirements for beet raw materials are determined by its physical condition (dried or fresh pulp), the need to achieve the quality of the final product from it, as well as the level of efficiency of mass transfer and hydromechanical processes of pectin extraction [3, 4]. They are analyzed in [3-6] and provide for the following conditions:

for use in pectin production pulp should be obtained by processing biologically ripe, healthy beets, mainly late digging;

fresh pulp must be further processed before drying to reduce the content of soluble fiber;

drying of pulp should take place in mild temperatures with the use of hot air as a drying agent;

the raw material must be homogeneous with respect to its particle size distribution.

Methods of preliminary preparation of pectin-containing raw materials and, in particular, beet pulp have been developed. Two methods have been proposed for the maximum extraction of pectin-based substances from beet raw materials [7-10].

The first method is the maximum removal of cell juice by grinding the root into a pulp with subsequent extraction under conditions that prevent denaturation of protoplasmic proteins, followed by hot extraction and pressing. This method allows to remove a large number of ballast substances, including protein. The second method involves the removal of ballast substances from beet pulp by grinding and additional extraction followed by pressing. This method is easier to organize its implementation. Preparation of beet raw materials by these methods requires at least two pressing operations.

There is a way to prepare fresh pulp by rinsing it with an electroactivated water system or acidified water, which makes it possible to free the pulp from excess soluble substances and remove

the buffering of beet tissue. When drying acidified pulp at elevated temperatures, partial hydrolysis of protopectin occurs, which allows the use of mild hydrolysis-extraction modes [9].

Positive results of preliminary squeezing of swollen dried beet pulp are given in [7]. This treatment of raw materials helped to increase the ability to gelate extracted pectin (by an average of 42%) and increase the yield of alcohol-precipitated pectin (by 35… 80%).

Determinant in the technological process of preparation of high quality raw materials is the method of drying. In the process of drying beet pulp, the temperature in the raw material should not exceed 85 ° C and the surface of the particles should not burn. Increasing the temperature in the raw material from 85 ° C to 130… 140 ° C leads to the loss of pectin from 29.0 to 26.7%, which is associated with thermal destruction of pectin [11, 12]. For beet pulp to be stored, the humidity should not exceed 14%.

Existing pulp drying regimes do not provide the required temperature parameters and do not meet the requirements for the use of a drying agent. When drying beet pulp on tumble dryers, the initial temperature of the coolant (fuel gases) is 575 ± 75 ° C, the final 90 ± 10 ° C, the process duration is 1-1.4 hours.

The kinetics of extraction of target components from plant raw materials is largely determined by the geometric shape and size of its particles. When preparing the pulp it is necessary to pay attention to the granulometric composition, in order to maximize the efficiency of the processes of extraction of pectin, to carry out fractionation by particle size. The optimal particle sizes of swollen beet pulp, which are 2… 6 mm, were determined [13, 14]. A method for obtaining dried beet grits has been developed, which involves a 6-fold reduction in the content of sugar and other fiber substances of the pulp due to its washing and deep squeezing. Drying of pulp is carried out with hot air, then granulated, and before use it is crushed and fractionated [7].

Extraction of pectin. Extraction of pectin consists of a series of technological operations, the implementation of which is the essence of a method of obtaining pectin.

Pectins of roots have a low ability to gelatation compared to fruit pectins (seed, subtropical and tropical), which are associated with low molecular weight, low methoxylation and high acetyl groups, without taking into account the hydrolysis of protopectin [12, 15, 16]. The results of research by scientists of the Institute of Organic Chemistry of the Kyrgyz Academy of Sciences have shown that the quality of pectin from beet pulp and, above all, its ability to gelatation, depends on the condition of the pulp - dried or fresh [17].

During hydrolytic processing of raw materials, protopectin is most destructured, hemicellulose is less destructured, and fiber undergoes insignificant changes. Hydrolysis of the protopectin complex consists of two stages: cleavage of bonds between chains of protopectin macromolecules with other components of the cell wall and hydrolysis of polymer chains of protopectin to form decomposition products with different molecular weights [18, 99]. Therefore, the hydrolysis conditions should provide for the cleavage of intermolecular bridges of protopectin with metal ions (Ca^{2+}, Mg^{2+}, etc.) and prevent the rupture of glycosidic and ether bonds of the pectin molecule.

The catalysts for hydrolysis are hydrogen ions (or hydroxonium). Mineral, organic acids and alkalis can be used as hydrolyzing agents. The catalytic action of hydrogen ions leads to changes in pectic substances depending on the temperature and pH of the medium. Methyl and acetyl esters are saponified at low pH values, and glycosidic bonds are broken when the temperature rises. When the process is catalyzed by hydroxyl ions, acetylether groups are saponified faster, and degradation of pectin macromolecules is observed. [19].

A necessary condition for the extraction of pectin from plant raw materials is the transfer of protopectin into a soluble state with

its subsequent extraction. The ability of raw materials to hydrolyze does not depend on temperature and pH, but is determined primarily by the type of raw material (fresh, dried, swollen), tissue morphology and chemical composition [7, 8, 9, 65, 66]. The influence of temperature and pH takes place in the change of the rate of reaching the state of intermediate equilibrium with the catalytic participation of H^+-ions. The rate of hydrolysis is determined by the diffusion of the hydrolytic factor into the tissue and the nature of the interaction of protopectin with it. It is directly proportional to the concentration of hydrogen ions in the polymer and the number of functional groups to be hydrolyzed. Thus, the chemical nature of beet protopectin necessitates harsh hydrolysis conditions (high temperature and low pH) [1].

Thus, the hydrolysis of protopectin is an internal process and is determined by the following main factors: physicochemical properties of raw materials, morphological structure of plant tissue, type of hydrolytic factor, temperature, pH value and process duration. The hydrolysis process does not depend on the ratio of solid and liquid phase masses, size and shape of particles. Extraction of soluble substances occurs as a result of their transfer inside the particle and due to convective diffusion into the volume of the external liquid [8, 20-26].

Based on the main provisions of the theory of mass transfer in the solid-liquid system, the speed of extraction of pectin from plant tissue depends on the following factors: the driving force of the process, particle size of raw materials, temperature, the ratio of the mass of the extractant and the particles of raw materials, the speed of the phases, the nature of the relative motion of the solid particles and the extractant [44].

Existing schemes provide for the compatibility of hydrolysis and extraction processes. Thus, hydrolysis-extraction of pectin from dried beet pulp is carried out at a concentration of hydrochloric acid of 1.1… 1.5%, the temperature of the hydrolysis mixture 75… 76°C,

the ratio of solid and liquid phases 1: (15… 16) for 2 h [27]. The following modes of hydrolysis-extraction are given in [12, 15]: the concentration of hydrochloric acid solution in the extractant is 1.3… 2.0%, hydromodule 1:20, temperature 70 ° C, duration 2.0… 2.4 h.

A technological scheme was implemented at the Gaisinsky Pectin Plant, where the hydrolysis process was separated and carried out at a relatively low phase cost ratio. Extraction took place in a step-by-step direct-flow mode [1, 28].

Extracts obtained by these regimes have a low pH value. Such technological schemes provide a stage of neutralization with 25% ammonium hydroxide solution [1, 29].

The above technologies require equipment and communications with high acid and corrosion resistance [20]. Modes of acid-thermal hydrolysis lead to demethoxylation and depolymerization of the pectin molecule [12, 15].

The "Pectin" Association has developed a method for producing pectin using electroactivated water. The exclusion of mineral acids allows the use of standard equipment of the chemical and food industries, to improve the environmental conditions of production. Pectin extract does not require additional purification and can be used directly for food production [9, 20]. The disadvantage of this method is the low yield of pectin and rapid wear of the membranes to obtain the extractant.

A promising direction in the extraction of pectin from the protopectin complex is the use of highly specific enzyme preparations. Aimukhamedova and staff of the Bach Institute of Biochemistry [29, 30] developed a method for producing pectin using a complex of enzymes from the fungus *Geotrichum candidum*, which contain cellulase and hemicellulase. Plant raw materials are treated with an enzyme preparation, partially free of pectolytic enzymes; this results in the cleavage of pectin bonds with cellulose and cell wall proteins and the release of low-degraded pectin. The

advantage of the method is the simplicity of hardware design, low-speed technological process, high yield of low-degraded pectins [29].

The use of native cellulase, as well as cellulase preparations with a high degree of purification from pectinases allow to obtain the structural elements of pectins - galacturonic acid and other carbohydrates [30].

The method of pectin production by freezing-defrosting of raw materials with subsequent enzymatic hydrolysis of protopectin in aqueous medium at a ratio of 1: 1 involves the destruction of cell walls. The amount of enzyme preparations (celoviridine, cellogeotrichin, cellobasidine) was 0.1 ... 0.3% by weight of raw materials. The low yield of pectin is explained by imperfect purification of enzyme preparations from pectinases [31].

Deposition, purification, drying of pectin. Theoretical bases of coaculation of pectin substances and results of researches of optimum conditions of deposition are stated in works [1, 8, 18, 17, 32, 33].

Concentration is carried out in vacuum evaporators, ultramembrane filtration units [1, 34, 89]. A method of concentrating pectin extract using beet grits is described [7].

Technological schemes provide for the precipitation of pectin from the extract with salts of polyvalent metals and organic compounds (aliphatic alcohols). According to the Krasnodar scheme, pectin is precipitated with aluminum chloride at pH = 6.0 ... 6.5. The obtained pectin-aluminum coagulate is a dark gray precipitate with a humidity of 97-98%. After pressing, the pectin is ground on a hammer grinder and sent for cleaning. Purification of coagulate is carried out in 4 stages with ethyl alcohol [35, 36]. Foreign productions also have technologies using aluminum ions for pectin precipitation; the coagulation process is carried out at pH = 4.0; aluminum ions are removed by washing with acidified isopropanol (HCl, pH = 1.0) [37, 38]. Purified pectin with a humidity of 48-50% is dried in vacuum dryers of the shelf type at an air temperature of 55 ... 65 ° C and a vacuum of 400 ... 500 mm Hg. for 5 ... 6 hours to a

final humidity of 14.0%. Studies have been conducted on the use of calcium chloride as a precipitant and incomplete deposition of pectin was found [39].

Most technologies use ethanol to precipitate pectin [1]. It is advisable to purify and concentrate the pectin extract. Different methods are used for purification: hydromechanical (filtration, settling, centrifugation), electrochemical (electrodialysis cleaning, electric field cleaning), ion exchange (cleaning with ion exchangers) [1, 40, 41].

Foreign companies produce a wide range of pectins with specified properties for use in various industries of food, cosmetics, pharmacology, medicine, etc. To do this, pectin, mainly apple or citrus, is subject to additional acid, alkaline or enzymatic treatment. Low-esterified pectin is obtained by such methods. Amidated pectin is obtained by treating pectin extract with ammonia gas [2, 42].

Physico-chemical characteristics of commercial pectin are regulated by DSTU 6088:2009 and provide a pectin content of not less than 50%, a strength of 2% gel not less than 300 mm Hg, total ash content not less than 3.5%, humidity not more than 14% [43].

NUHT scientists have developed a technology for drying concentrated pectin extract in a spray dryer. Pectin extract for such drying should be obtained using food acids or electroactivated aqueous system. The content of the target substance in the product is about 30% [68].

Existing technologies for the production of beet pectin mainly use dried beet pulp. Beet tissue of such production is subjected to prolonged temperature exposure, which results in the loss of pectin and their destruction. Thus, in the diffusion apparatus pre-scalded shavings are 60 ... 90 minutes. at a temperature of 60 ... 85 ° C. Drying of pulp occurs at a temperature of 100 ... 140 ° C for 60 ... 100 minutes. Pectin extracted from the such pulp generally has poor solubility, low molecular weight and gelling ability.

Many researchers have proven the benefits of using fresh pulp to produce high quality pectin. However, given the short shelf

life of fresh pulp, its processing into pectin is possible in the presence of a pectin shop at a sugar factory or near it.

In order to obtain beet pectin with high quality properties, special preparation of raw beets is required.

2.2 The structure of beet root tissue and its physicochemical characteristics

Sugar beet (*Beta vulgaris*) is the main raw material for sugar production in Ukraine. In the 50-60 years of the last century, beets were also one of the constant raw materials in the alcohol industry.

Based on the submicroscopic structure, beet tissue is considered as a bundle-fibrillar structure with two types of pores: narrow homocapillary (between bundles of cellulose macromolecules) and large heterocapillary (gaps between fibrils), which connect with each other and form a continuous transition. [22].

The root consists of a central rod and several rows of vascular-fibrous bundles, which alternate with parenchymal tissue. In cross section, the vascular bundles have the form of concentric rings, in longitudinal section - in the form of cones that are nested in each other, separated by lighter layers of parenchyma. The parenchymal tissue, which makes up about three-quarters of all beet root cells, alternates with vascular bundles and fibers. It is made up of cells that contain sugar-containing cell sap. The vacuoles of mature beet cells spread over almost its entire volume, as a result of which the protoplasm adheres tightly to the walls in the form of a thin layer. The main component of the protoplasm is a protein, which under the action of heat, acids, alkalis denatures, and through the protoplasm can penetrate all the substances contained in cell juice [22].

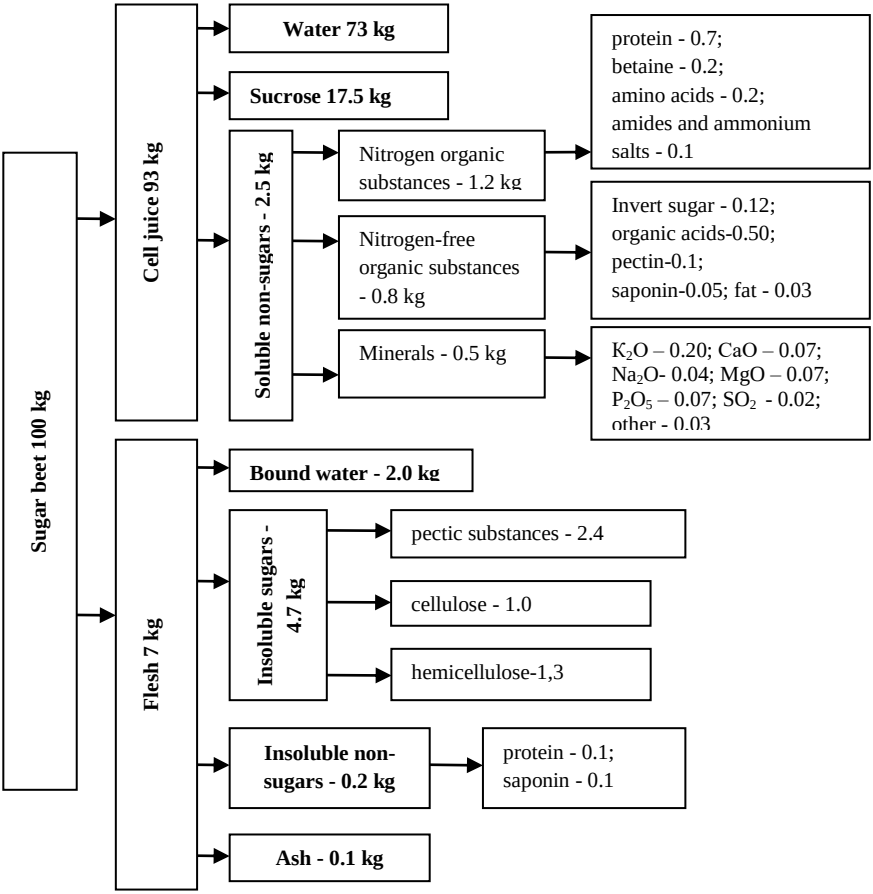

Figure 2.1 - Chemical composition of sugar beet roots [22]

Beet tissue is a quasi-solid body of cellular structure. In fresh form, it is a semi-liquid mass, the shells of which are connected by a so-called intercellular space. Cell membranes are formed during growth from a complex of substances that form the basis of all plant tissues - cellulose, hemicelluloses, pectin, proteins and others.

The chemical composition and technological qualities of sugar beet depend on the variety, growing conditions, method of harvesting, storage. Non-sugars are found in both juice and pulp. However, pectin substances dominate the in pulp [22, 48].

The direct raw material for pectin production is sugar-free beet pulp.

2.3 Structure, chemical composition and physicochemical properties of beet pulp

By its structure, the pulp is a complex capillary-porous body. Its cells and intercellular cavity are filled with water with low sucrose content. Relationships of moisture with substances in the pulp can be attributed to physicochemical (adsorption and intracellular) and physico-mechanical (capillary and wetting). Moisture is not completely removed during pulp pressing [48].

Beet pulp tissue consists mainly of polysaccharides (66.3%), the main components of which are the following monosaccharides: glucose (21.7%), galacturonic acid (18.9%) and arabinose (17.3%). Other carbohydrates, except galactose (4.3%), are found in small quantities (about 1.5%) [53, 63].

Cellulose molecules are formed by linear chains of 1,4-linked glucose residues. Monosaccharide units have a C1-pyranose ring conformation with a well-defined spatial arrangement of hydroxyl groups, which determine different types of intra- and intermolecular bonds [98].

The sugar content in dry pulp depends on the modes of pressing and the design of the press and can be 1.5 ... 2% [22]. There are data on the content of sucrose in samples of dry pulp at the level of 1% [48]. Sucrose is easily disintegrate under the action of acids, alkalis, oxidants and enzymes. At thermal influence various substances are formed - caramels, which determine the color of the pulp [50].

Darkening also causes the presence of melanins - products of enzymatic oxidation of polyphenols of beet juice and melanoidins - products of the reaction of monosaccharides with amino acids [49, 52]. Melanins are formed in the presence of oxygen with the participation of the enzyme phenoloxidase [51, 54]. Melanoidins are

formed by the interaction of amino acids with furfural and oxymethylfurfural, which are products of carbohydrate decomposition [52]. It should be noted that pectin production is interested in the use of light pulp.

Arabinose, as the other main neutral carbohydrate, is connected mainly by 1,5 - and 1,3,5 - bonds, and is also present in the free state. Small amounts of 1,3-bound highly branched araban residues were also found. This is a typical example of an arabinan [73, 74, 86, 93].

Galactose residues are bound by 1,4-glycosidic bonds, but sometimes in 1,3- and 1,6-bonds and form the so-called arabanogalactans type 1 and type 2. The latter are also found in other cell walls, indicating on the prevalence of such polymers in plant tissues [75, 76].

Rhamnose is present in the linear and lateral chains of pectin (1, 2, 4-linked residues) [76]. Xylose residues are 1,4-linked or free. Mannose was found only bound at position 1.4 [54].

Xylanes, mannans, arabinans and galactans are part of hemicelluloses - a group of polysaccharides that are highly soluble in aqueous solutions of alkali metal hydroxides and relatively easy ability to hydrolyze aqueous solutions of acids [55, 77].

Lignin is contained in pulp in small quantities (1.8%). It is a natural polymer with an irregular mesh or three-dimensional structure that forms the cell walls of plants. It plays the role of an inlaid substance that binds cellulose and hemicellulose fibers [54].

The protein content is 8% [75, 77]. Protein substances are connected with polysaccharides by ester bonds. In the pulp of sugar beet production proteins are significantly denatured and have hydrophobic properties. Pectic substances easily interact with amino acids to form pectates and pectinates. The interaction of pectin substances with proteins leads to the formation of complex preservatives and insoluble complexes [49, 84]. The ash content is -

8.4%. Veshtan and others for pressed pulp give lower content of protein, galacturonic acid, arabinose and higher content of ash [78].

Methanol and acetic acid are contained in a fairly high amount (2.3% and 3.6%, respectively). The carboxyl groups of galacturonic acid are esterified with methanol and the level of metaxylation is 69 units of methanol for every 100 galacturonide molecules. Hydroxyl groups are esterified with acetic acid residues and the level of acetylation reaches 60.8% [53]. The same level of methoxylation was determined for pectin extracted from beet pulp, while the number of acetyl groups in the pulp was almost twice as high, which can be explained by the connection of acetic acid with other structural polymers [94].

Beet pulp contains about 1.3% phenolic acids. Ferulic (0.93%), hydroxybenzoic (0.17%), syringic (0.09%), vanillin (0.06%) and fumaric (0.06%) acids were identified. According to Marshall and Tibaut, pectins extracted from beet pulp contained small amounts of ferulic acid (0.2-0.7%) associated with neutral side chain sugars [45, 94]. Ferulic acids have also been found in spinach pectins and wheat pentosans [46]. Ferulic acids are thought to be involved in cross-linking reactions in cell walls [47].

Physico-chemical properties of beet pulp depend on the structure and ratio of its constituent components.

The structure of the pulp determines its ability to diffuse transfer of substances. With regard to beet tissue, it is noted that the behavior of individual structural components is determined by their relationship with cellulose. Low-molecular substances easily penetrate into amorphous regions, and penetration into crystalline ones is limited. It is the state of the pectin-cellulose complex that determines the diffusion conductivity of beet tissue [8]. The rate of hydrolysis is determined by the diffusion of the agent into the tissue and depends on the content of functional groups of structural components.

Diffusion permeability of beet raw materials is the main criterion of all mass transfer phenomena that take place in the structure at certain stages of its processing. The amount of tissue permeability is affected by mechanical, thermal, chemical, electrical and other actions. At various actions properties of beet tissue change, and these changes occur both in amorphous, and in crystalline phases of structure. The diffusion coefficient of soluble pectin substances in the process of extraction with water from hydrolyzed pulp varies over time exponentially from $29.16 \cdot 10^{-11}$ to $1.4 \cdot 10^{-11}$ m^2/s [8, 58], which is several orders of magnitude lower than the permeability of cell membranes in in relation to clean water (10^8 m^2/s) [59].

Physico-chemical changes in the tissue, which in turn lead to changes in the mechanical and diffusion properties of the latter, may be the result of hydrothermal treatment [62], freezing - defrosting [60], hydroacoustic disintegration.

Beet fabric combines biopolymers with different affinities for water. The ratio of the components of the pulp determines such an important characteristic of the raw material as moisture holding capacity. Pectic substances and some hemicelluloses belong to the category of hydrophilic colloids. Cellulose has a large number of hydroxyl groups and a developed system of thin submicroscopic capillaries, which determines its ability to absorb and retain water. Lignin is the least hydrophilic. For dried pulp, the moisture holding capacity averages 26.2 g of water per 1 g of dry matter [78]. Moisture during swelling of the dried material is the sum of osmotic and immobilized moisture. Depending on the ratio of these forms of moisture binding, the structural and mechanical properties of the material change [84]. The basis for changing the ratios are the phenomena of sorption and desorption - complex processes: adsorption, capillary condensation and osmotic absorption of moisture by micelles of the material [56].

Sorption activity of beet tissue is determined by the ability of tissue components that have cyclic groups to form stable chelated complex compounds. To a large extent, these properties are

explained by the presence of pectin substances, which can form insoluble complex compounds, for example, with organic toxins - phenols, amines, etc. [49].

Plant tissue has ion exchange properties. This is explained by the fact that at the interface of the solid phase with aqueous solutions there is almost always a special arrangement of electric charges - a double electric layer. It consists of inner and outer shells. Ions that are part of the solid phase form the inner shell. Opposite ions, which are not part of the solid phase, and which are associated with it by electrostatic forces, form the outer shell. They are in dynamic equilibrium with the ions of the solution and are exchanged in equivalent quantities for ions of the same sign that are in solution. Cation exchange properties are due to the presence of carboxyl and phosphoric acid groups, anion exchange - the presence of amino groups [32].

Pectin production uses both fresh and dried beet pulp. The first refers to colloidal capillary-porous materials, the second - to capillary-porous. Both types of raw materials, based on morphological features, are isotropic [57].

Pulp is considered as a coarse dispersion with a dispersion liquid phase, which in the processes of mass transfer can significantly change its physicochemical composition.

2.4 Biochemical utilization of sugars

Requirements for pectin production to raw materials include a minimum content of ballast substances relative to pectin and maximum preservation of the native structure of the pectin molecule. In the process of preparation of beet raw material it is necessary to free plant tissue from its soluble components, to convert some insoluble protein substances into disaggregated soluble form and at the same time preserve quantitatively and qualitatively pectin substances.

Extraction is the most common method of extracting soluble substances from plant raw materials [23]. It is proposed to grind

sugar beet roots into chips, to extract soluble substances with water at a temperature of 30 ° C in a periodic mode with simultaneous utilization of sugars by targeted fermentation of the latter on ethyl alcohol by culture of alcoholic yeast *Saccharomyces cerevisiae*.

To implement the scheme of simultaneous extraction and utilization of sugars, it is necessary, on the one hand, to provide conditions for maximum transfer of soluble substances from sugar beet tissue into water, and, on the other hand, to create a full environment for alcoholic yeast to produce ethanol for use in stages of precipitation and purification of pectin coagulate.

Most soluble substances are found in cell sap, which is contained in the vacuoles of the plant cell of root crops. Prerequisite for the extraction of sugars is the destruction of the protoplasm of the vacuoles. Denaturation of protoplasm by heating, which takes place during juice production in sugar production, leads to loss and partial destruction of pectin. Therefore, the task of the research was to carry out the most complete removal of soluble compounds without the action of elevated temperature.

In the process of cutting beets there is mechanical damage to cell walls and membranes surrounding the vacuole. The number of damaged cells depends on the degree of grinding of beet tissue, which is determined by the size of the chips. Studies on the sugar removal of beet chips, the length of 100 g of which was 15 m, showed that at a temperature of 12 ° C for the first 4-5 minutes washed away 1/3 of sucrose [23, 64].

For pectin production, the dependence of the yield of alcohol-precipitated pectin substances and their quality on the particle size of the pulp during their hydrolysis-extraction has been experimentally established [35]. The given radius of chips at which the yield and quality of pectin are optimal is $(0.8 ... 1.2) \cdot 10^{-3}$ m, which corresponds to a length of 100 g of shavings 26 ... 40 m. Grinding roots into shavings of such sizes, with up to 60% of sugars can be removed from beet tissue without heat treatment. Given the

periodic regime, the amount of sucrose washed from shavings depends on the amount of extractant, ie the ratio of the mass of chips and water. The mash obtained by mixing beet chips with water contains most of the substances necessary for the cultivation of alcoholic yeast.

To determine the technological parameters of biochemical preparation of beet raw materials, laboratory studies were conducted. Test samples of sugar beet roots contained 20.5% solids and 18.0% sucrose, pH = 7.08. The roots were cut into chips, 100 g of which were 37 m long, mixed with water in the ratio of chips: water 1.5: 1, 1: 1, 1: 1.5 and 1: 2 and sown with a culture of alcoholic yeast *Saccharomyces cerevisiae* race K- 7. The amount of added water should ensure the manufacturability of the environment with minimal dilution. At the beginning of fermentation, the cell content was 30 million / ml. Main fermentation temperature 32 ° C, fermentation 28 ° C. The results of experimental data are presented in table 2.1.

Table 2.1 - **Technological indicators of the fermentation process**

Indicators	Chip: water ratio			
	1,5 : 1	1 : 1	1 : 1,5	1 : 2
Solids content,%				
Initial	12,3	10,25	8,2	6,2
Final	6,65	5,5	4,3	3,5
Sucrose content in сріпзі, %				
Initial	18,0	18,0	18,0	18,0
Final	0,54	0,42	0,37	0,30
pH				
Initial	7,08	7,09	7,12	7,12
Final	4,85	4,76	4,66	4,54
Accumulation CO_2, g/200 g	10,14	8,65	6,99	4,34
Alcohol content,% vol	8,02	6,84	5,53	3,50

The obtained results showed that the dilution of the crushed mass of root crops in the ratio of 1: 1 and 1: 1.5 have good manufacturability with a sufficient level of ethanol accumulation for its further isolation.

Studies have shown that the fermentation of sugar-free beet chips to a sugar content of 0.4% occurs in 24 ... 46 hours. Periodic stirring is required to speed up the extraction and to distribute the soluble substances evenly in the volume of the fermenter. In fig. 2.2 presents the dynamics of carbon dioxide accumulation during fermentation of beet mash without stirring and with stirring. With periodic stirring, the duration of the process is reduced from 46 to 24 hours. With stirring, approximately 50% of the sucrose from the chips is extracted and disposed of in the first 5 hours of fermentation. The gradual decrease in the rate of sugar removal can be explained by the fact that the sugar is extracted from the inner layers of chips, which did not suffer mechanical damage during the grinding of roots. Diffusion of soluble substances from intact cells at low temperatures becomes possible by creating a gradient of sugar concentrations and due to the accumulation in the environment of ethanol, carbon dioxide and organic acids. It is known that alcohol solutions affect the state of plant cell membranes by increasing its permeability [36]. Carbon dioxide dissolves to form carbonic acid and increases the acidity of the environment [90].

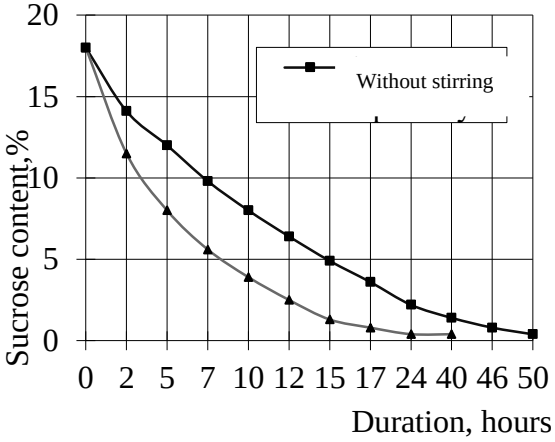

Figure 2.2 - Dynamics of sucrose utilization from chips during fermentation of beet mash

The presence of a branched chip surface in beet mash contributes to the intensive release of carbon dioxide. Carbon dioxide is adsorbed on chip particles and pulp flotation occurs. Once on the surface, it comes into contact with oxygen and darkens as a result of catalytic oxidation of polyphenolic compounds with the enzyme phenoloxidase. This, in turn, is reflected in the color of the target product - pectin. Stirring promotes the separation of carbon dioxide and evenly distributes the solid phase in the liquid. Soluble carbon dioxide in the mash interferes with oxidative processes and the pulp is white.

The mash obtained by mixing beet chips with water contains a sufficient number of necessary substances for the cultivation of alcoholic yeast, namely soluble carbohydrates, nitrogen and minerals. It is necessary to choose a culture of alcoholic yeast, which would most efficiently utilize soluble carbohydrates of beet mash. Criteria for assessing alcohol fermentation in the selection of strains of microorganisms determined the accumulation of alcohol, the depth of fermentation of sugar beet mash and the rate of fermentation.

To solve the problem of simultaneous extraction and utilization of sugars from sugar beet tissue, comparative studies were conducted to select the culture of alcoholic yeast. 3 monocultures of *Saccharomyces cerevisiae* of races B, M-5 and K-7 were studied.

Analysis of literature sources showed that the processing of sugar beets into alcohol with the extraction of diffusion juice was carried out using yeast races, which ferment sucrose well (YA, L, B, M). But the best was race V, which did not require additional mineral fertilization of diffusion juice and has long been successfully used in industrial conditions [69].

Beet mash contains 0.1… 0.5% raffinose, which can be fermented by yeast strains that have the enzyme α-galactosidase (melibiasis) and are able to hydrolyze and utilize this trisaccharide. Such requirements are met by hybrid strains of *Saccharomyces*

cerevisiae G-67 and G-73, which are characterized by high activity, deep fermentation of sugar beet mash and are effectively implemented in sugar beet alcohol production plants [70, 92].

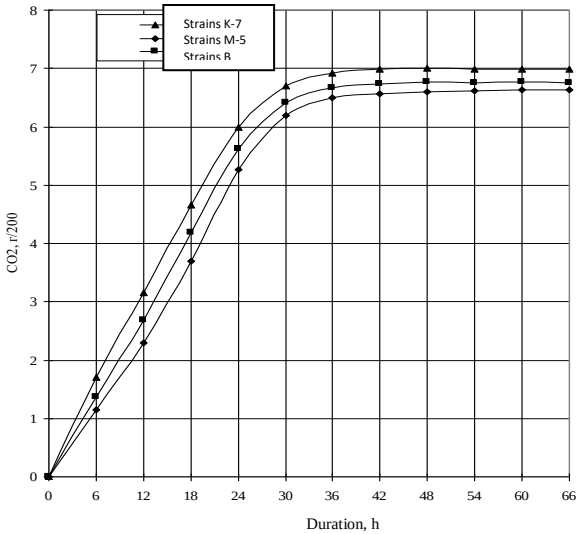

Figure 2.3 - Dynamics of carbon dioxide evolution during fermentation of beet mash by different strains of yeast

Saccharomyces cerevisiae K-7 - modern effective strains with melibiasis activity, selected in "Ukrspyrtbioprod", have a high specific growth rate, quickly form ethyl alcohol and deeply ferment beet mash.

Sugar beet roots were crushed and mixed with water in a ratio of 1: 1.5. At a temperature of 30 ° C was set sowing yeast based on the calculation of 100 million cells per 1 ml of beet mash. Fermentation of beet mash was carried out with different strains of the yeast *Saccharomyces cerevisiae.*

According to the obtained results, strains of *S. cerevisiae* B, *S. cerevisiae* G-67 (G-73), *S. cerevisiae* K-7 provide high technological indicators, which are determined by the accumulation of CO_2, unfermented sugar content and concentration of alcohol in

the fermented wort. Strain *S.servisiae* K-7 dominates in activity at high concentrations of alcohol in the fermented wort.

Chemical and technological parameters of mature fermented wort during fermentation of beet mash by different strains of the yeast *Saccharomyces cerevisiae* are shown in table 2.2.

Table 2.2 - **Chemical and technological parameters of mature fermented wort**

Yeast strain	**pH of fermented wort**	**The content of reduced sugars in the fermented wort, %**	**Accumulation CO_2, g/200g**	**Alcohol content, % vol.**
S.cerevisiae B	4,86	0,074	6,95	5,50
S.cerevisiae Г-67 (G -73)	4,89	0,09	6,74	5,37
S.cerevisiae K-7	4,87	0,072	6,99	5,53

In order to determine the composition of impurities in the fermented distillate, studies were performed by gas chromatography and determined the main components of fermentation products and the content of impurities in it: acetaldehyde - 1181 mg/dm^3, acetic ethyl ether - 112 mg/dm^3, methanol - 9.1 mg/dm^3, n-propanol - 100 mg/dm^3, isobutanol - 593 mg/dm^3, isoamyl alcohol - 958 mg/dm^3. The ethanol obtained from such a distillate can be used in the technological process in the subsequent stages of isolation and purification of pectin.

The results of qualitative and quantitative content of impurities in the fermented distillate are shown in table 2.3. The ethanol obtained from such a distillate can be used in the technological process in the subsequent stages of isolation and purification of pectin.

Table 2.3 - **Component composition of the fermented distillate**

№ п/п	Component of the fermented distillate	Mass fraction, mg/dm^3
1	acetaldehyde	1181
2	acetic ethyl ether	112
3	methanol	9,1
4	n-propanol	100
5	isobutanol	593
6	isoamyl alcohol	958

To implement the scheme of simultaneous extraction and utilization of sugars, it is necessary, on the one hand, to provide conditions for the diffusion of soluble substances, and, on the other hand, to create a complete environment for alcoholic yeast to produce ethanol for use in stages of deposition and purification of pectin coagulate.

Most soluble substances are found in the cell juice, which is contained in the vacuoles of the plant cell of root crops. Prerequisite for the extraction of sugars is the destruction of the protoplasm of the vacuoles. Denaturation of protoplasm by heating, which takes place during juice extraction in sugar production, leads to loss and partial destruction of pectin substances. Therefore, the task of the research was to carry out the most complete removal of soluble compounds without the action of elevated temperature.

In the process of cutting beets there is mechanical damage of cell walls and membranes surrounding the vacuole. The number of damaged cells depends on the size of the chips. Studies [57] on the sugar removal of beet chips, the length of 100 g of which was 15 m, showed that at a temperature of 12 ° C for the first 4-5 minutes washed away 1/3 of sucrose.

For pectin production, the dependence of the yield of alcohol-precipitated pectin substances and their quality on the

particle size of the pulp during their hydrolysis-extraction has been experimentally established [20]. The given radius of chips at which the yield and quality of pectin are optimal is (0.8 ... 1.2) • 10^{-3} m, which corresponds to a length of 100 g of shavings 26 ... 40 m. Grinding roots into chips of such sizes, with up to 60% of sugars can be removed from beet tissue without heat treatment. Given the periodic regime, the amount of washed sugar from chips depends on the amount of extractant, ie the ratio of the mass of chips and water.

2.5 Influence of enzymatic processing of beet raw material on protein content in pectin

Sugar beet contains a significant amount of protein (0.7%), some of which is converted into pectin. Yeast assimilates nitrogen in the form of free amino acids and ammonium salts. It was found that the direct assimilation of amino acids, which involves their use as a whole, ie both nitrogen and carbon residue, reduces the cost of sugars in the generation of yeast and thus increases the yield of ethanol during fermentation [91]. Increase the number of amino acids in the substrate is possible due to the destruction of protein [81, 85].

To reduce the protein content in the finished product - pectin, as well as to provide yeast with nitrogen nutrition, studies were conducted on the treatment of beet mash with proteolytic enzyme preparation neutrase of company Novozim (Denmark).

Beet pulp was mixed with water in a ratio of 1: 1.5, the enzyme preparation was set per unit of activity at the rate of 0.024; 0.028; 0.035 prs/g of raw material and kept at a temperature of 45… 50 ° C, which is optimal for the enzyme preparation, for 30 minutes Beetroot mash without protease treatment was used as a control. The results are shown in table 2.4.

Based on the results obtained, it was found that treatment with the enzyme preparation of protease not only increases the

fermentative activity of yeast, but also increases the ethanol content in the fermented wort by 0.1… 0.25% compared with the control.

Table 2.4 - **Chemical and technological parameters of mature fermented wort obtained using an enzyme preparation**

Concentration of protease, prz / g of raw materials	Allocation CO_2, g/200 g, in an hour				Accumulation of yeast cells, million CFU/ml, after an hour					Alcohol content,% vol.
	12	24	48	60	0	12	24	48	60	
Control	5,70	6,75	6,95	6,97	30	77	101	110	112	4,50
0,020	5,9	6,93	7,0	7,02	30	98	125	128	127	4,69
0,028	6,15	7,12	7,17	7,20	30	104	143	157	159	4,80
0,035	6,17	7,14	7,20	7,22	30	109	148	159	160	4,83

Subsequent studies have shown that the use of prostheses in the amount of 0.028 prz/g of raw materials provided a reduction in protein content in pectin by 41%. Increasing the amount of enzyme preparation did not give a tangible result.

Thus, studies have shown that treatment of beet raw material with protease enzyme preparation, which precedes the utilization of sugars by fermentation of the latter in ethyl alcohol, makes it possible to obtain pectin with less destructive changes in the molecule and reduce protein content in the final product.

Further research was aimed at elucidating the nature and amount of nitrogenous substances in pectin derived from fermented beet raw materials.

One of the main ballast compounds in beet pectin are proteins that can get into pectin from biochemically prepared beet

raw materials from two sources. The first source is beet raw material, which is characterized by a relatively high content of protein (0.7%), and most of them are in a state associated with the polysaccharide complex of the cell wall. Acid-heat treatment leads to denaturation of proteins, cell wall permeability increases and proteins are extracted. The modes of hydrolysis of protopectin do not lead to deep destruction of the protein molecule and at the stage of precipitation the proteins coagulate with pectin [84].

Alcoholic yeast is used in the biochemical preparation of beet raw materials. The fermentation process is accompanied by the growth of yeast biomass, yeast cells are adsorbed on the branched surface of beet tissue particles. Washing the fermented chips does not allow to completely separate the plant tissue from the yeast cells. Yeast can be the second source of protein in pectin, passing into it during extraction.

Studies have been performed to determine the likelihood of pectin contamination by the yeast protein fraction and the effect of proteolytic enzyme treatment on the quality of the final product.

Studies to determine the content of the protein fraction were performed in three samples:

- pectin obtained from fermented beet pulp;

- pectin obtained from fermented beet pulp, pre-treated with proteolytic enzyme preparation neutrase of company Novozim (Denmark);

- pectin from beet pulp which sugar-free by extraction (control).

The protein content was determined by the sum of amino acids, which was determined after complete hydrolysis of the protein by chromatographic method. This method also makes it possible to establish the complete amino acid composition of proteins in pectin samples. The results of studies on the content of amino acids and protein in pectin samples are shown in table 2.5.

Table 2.5 - **Amino acid and protein content in pectin**

Amino acids and total protein	Content, %		
	Contol	Sample I	Sample II
Lysine	0,6398	0,6436	0,3347
Histidine	0,2502	0,2496	0,1523
Arginine	0,2823	0,2819	0,1635
Oxyproline	0,8003	0,8218	0,5063
Asparagine	0,3615	0,3487	0,2093
Threonine	0,3401	0,3641	0,2330
Serine	0,4182	0,4025	0,2254
Glutamine	0,5559	0,5773	0,3271
Proline	0,3991	0,3871	0,2458
Glycine	0,2225	0,2273	0,1341
Alanine	0,3236	0,3140	0,2031
Cysteine	0,0298	0,0325	0,0194
Valine	0,2776	0,2682	0,1475
Methionine	0,0578	0,0566	0,0364
Isoleucine	0,1461	0,1328	0,0823
Leucine	0,3026	0,3064	0,1747
Tyrosine	0,4439	0,4235	0,2470
Phenylalanine	0,1754	0,1746	0,1048
Total protein	6,0267	6,0125	3,5467

According to the results of research, the protein content in pectin extracted from fermented raw materials does not differ from the protein content in the control sample. This indicates that in the process of hydrolysis-extraction lysis of yeast cells does not occur and their structural protein components do not pass into pectin extract.

Treatment of raw materials with an enzyme preparation reduces the amount of protein in pectin, in our experiments this reduction was 41%.

The amino acid composition of the protein fraction in pectin was determined, which allowed to assess its biological value.

Comparing the content of essential amino acids, their scores are determined. Thus, for lysine the score is 195%, threonine - 165%, phenylalanine and tyrosine - in the amount of 166%. The limiting amino acids were cysteine and methionine (score 42%), leucine (score 73%), isoleucine (score 55%), valine (score 89%).

The amino acid taurine, which plays a significant role in the human body, has been found in the protein fraction. It is found in the heart muscle, retina, skeletal muscle and blood cells.

In addition to nitrogenous substances, pectin ballasts include minerals. Further researches were carried out for clarification of a mineral component of pectin.

2.6 Accumulation of toxic elements in the process of extraction of pectin from biochemically treated raw materials

One of the most important properties of beet pectin is its complexing ability. Beet pectin is a substance with a high ability to complexation, and the binding of polyvalent metal ions occurs in a wide range of pH. This property of pectin determines its use for preventive and therapeutic purposes for groups of the population in contact with radionuclides, salts of heavy metals, pesticides [80, 100].

However, the high binding activity of beet pectin makes it difficult to obtain it within acceptable limits for toxic elements. This is due to the fact that in the production process there is an interaction of raw materials, intermediates with technological environments and equipment that contain a significant amount of metal ions. In the final product - dry pectin, the concentration of heavy metals can significantly exceed the standard level.

Therefore, it was advisable to conduct research on the accumulation of toxic elements at the stage of biochemical preparation of raw beets and pectin from such raw materials, as well

as to compare the levels of accumulation of toxic elements in raw materials and pectin in various methods of sugar removal.

In the laboratory, the migration of heavy metals during the extraction of pectin from beet pulp, sugar-free by extraction, and from pulp, sugar-free during simultaneous extraction and alcoholic fermentation was studied.

Sugar remove from the pulp by extraction was performed with distilled water (t = 60 ... 70 ° C), after which the sugar-free pulp was kept for 24 hours at room temperature in the model environment - a solution of salts of heavy metals, the composition of which is given in table 2.6.

Table 2.6 - **The content of heavy metal salts in the model environment**

№	Salt	Salt content, mg %	Metal ion content, mg %
1	$ZnCl_2$	4,67	2,23
2	$Pb(NO_3)_2$	2,67	1,31
3	$CuSO_4 \cdot 5H_2O$	2,67	0,68
4	$ZrOCl_2$	4,00	2,04
5	$CdSO_4$	4,00	2,20
6	$CrCl_3 \cdot 6H_2O$	4,00	0,78

To free beet tissue from sugars during simultaneous extraction and fermentation, sugar beet root pulp was mixed with the above model medium in a ratio of 1: 1.5 and inoculated with Saccharomyces cerevisiae alcohol yeast culture race K-7. With periodic stirring, the fermentation process lasted 60 h at a temperature of 32… 33 ° C.

Control experiments were performed in parallel without the introduction of heavy metals into the environment. The content of heavy metals was determined by atomic adsorption method in the raw material, sugar-free pulp, source yeast, yeast after fermentation and pectin. The results of studies on the content of heavy metals in the studied samples of raw materials and pectin are presented in table 2.7.

Studies have shown that the levels of accumulation of heavy metals in the pulp, removal of sugar by various methods, range from 0.5% for Zn^{2+} to 40% for Pb^{2+}. It should be noted that washing the pulp after fermentation does not reduce the content of cations in it.

The values of the content of heavy metals in pectin from different pulp and spent yeast are significantly different. The data are presented in Fig. 2.4.

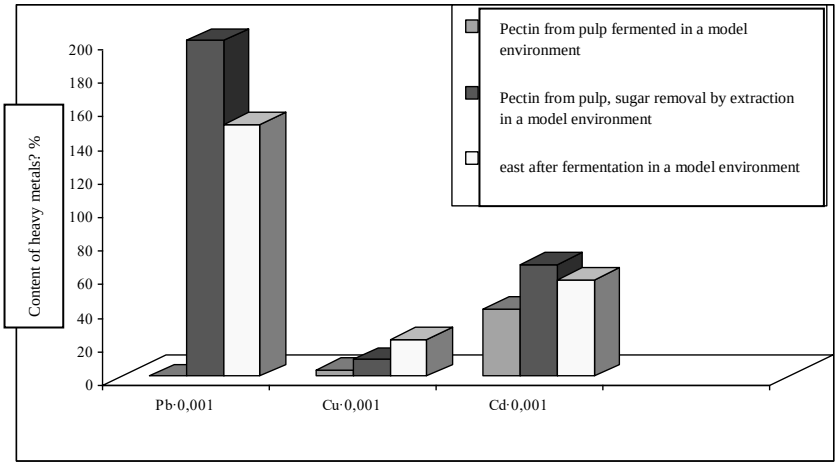

Figure 2.4 - Content of heavy metal ions in pectin and yeast

Table 2.7 - **Content of heavy metals in raw materials, pectin and yeast**

№	Sample	The content of heavy metal ions, %											
		$Zn^{2+}\cdot10^{-3}$		$Pb^{2+}\cdot10^{-4}$		$Cu^{2+}\cdot10^{-4}$		$Zr^{2+}\cdot10^{-3}$		$Cd^{2+}\cdot10^{-3}$		$Cr^{2+}\cdot10^{-4}$	
		Control	Experiment	Control	Experiment	Control	Experiment	Control	Experiment	Control	Experiment	Control	Experiment
1	The original pulp of sugar beet roots	1,1		0,1		0,75		0,15		0,08		0,12	
2	Fermented pulp not washed	0,5	20,1	0,25	400,0	2,1	20,2	0,12	6,24	0,1	40,0	1,5	30,0
3	Fermented pulp washed	0,5	20,0	0,25	400,0	2,1	40,1	0,12	6,0	0,1	40,0	1,5	24,0
4	The pulp sugar removal by extraction	2,0	20,0	1,3	240,0	2.0	32,0	0,16	10,0	0,7	40,0	0,33	32,0
5	Pectin from fermented pulp	2,6	50,0	2,6	20,0	3,3	40,0	0,2	1,5	0,1	40,0	1,0	25,0
6	Pectin from pulp, sugar removal by extraction	4,0	49,0	50,0	2000,0	15,0	100,0	0,5	93,0	1,2	66,6	4,0	34,0
7	Initial yeast	1,4		6,2		3,2		1,4		0,4		1,1	
8	Yeast after fermentation	7,1	43,0	13,1	1500,0	4,3	220,0	0,6	93,0	1,4	57,2	1,1	86,0

The results on lead ions are the most significant. Thus, the content of Pb^{2+} ions in pectin from pulp sugar removal by extraction and aged in the model medium was 100 times higher compared to pectin obtained from pulp fermented in the model medium. The content of zirconium ions was $1.5 \cdot 10^{-3}$ % and $93.0 \cdot 10^{-3}$ % according to the above-mentioned pectin samples and differed from each other 62 times. Smaller differences were observed with respect to copper ions (the difference was 2.5 times), chromium ions (by 26.5%), cadmium ions (by 25%). The content of zinc ions in the studied pectin samples was almost at the same level.

Determined amounts of accumulated metal ions in fermented yeast showed their high binding activity. Yeast in the process of its vital activity is able to accumulate significant amounts of cations of heavy metals. In beet mash, a large number of yeast cells are adsorbed on the solid particles of the pulp, washing which does not lead to its separation from the yeast biomass. However, the metals bind strongly to the yeast and do not pass into the final product during the pectin extraction process. Such data coincide with the conclusions of researchers [108], who suggest using the property of yeast to accumulate metals for wastewater treatment.

In addition, it is known that the acidic reaction of the environment reduces the ability to complexetion of pectin [78]. The decrease in pH from 7.0...6.5 to 3.8...4.7 occurs during fermentation. It is likely that this factor also affects the level of accumulation of metal cations in pectin.

2.7 Hydrolytic cleavage of beet tissue protopectin

Neukom proposed several possible variants of chain formation through bridges between pectin molecules [79]:

1. Mechanical connection in cells or a network of filamentous micromolecules of pectin with each other.

2. Mechanical connection in cells of pectin molecules with other highly polymeric substances that are part of cell walls (cellulose, hemicellulose, lignin).

3. Formation of etheric bonds between hydroxyl groups of alcohols and other substances that are part of cell walls (cellulose, hemicellulose, lignin).

4. Formation of lactone bonds within a complex pectin molecule.

5. Formation of salt-like bonds between pectin carboxyl groups and major protein groups.

6. Bonds through polyvalent ions (Mg, Ca, Fe) between carboxyl groups of complex pectin molecules or between different primary valences of pectin chains.

7. Bonds due to secondary valences (with freely adsorbed substances, hydrogen bonds, bonds due to hydrated water, molecular adhesion, etc.) between pectin molecules and other substances in cell walls.

Some possible links between pectin molecules are shown below (Figure 2.5).

The structure and chemical composition of pectin substances determine the spatial shape of their molecules and the nature of interaction with other compounds. Pectic substances have been shown to have a structure with limited flexibility that is stabilized by hydrogen and hydrophobic bonds [95]. Pectin molecules have a predominantly filamentous structure and belong to the linear colloids with a molecule length of about 10^{-5} cm [96].

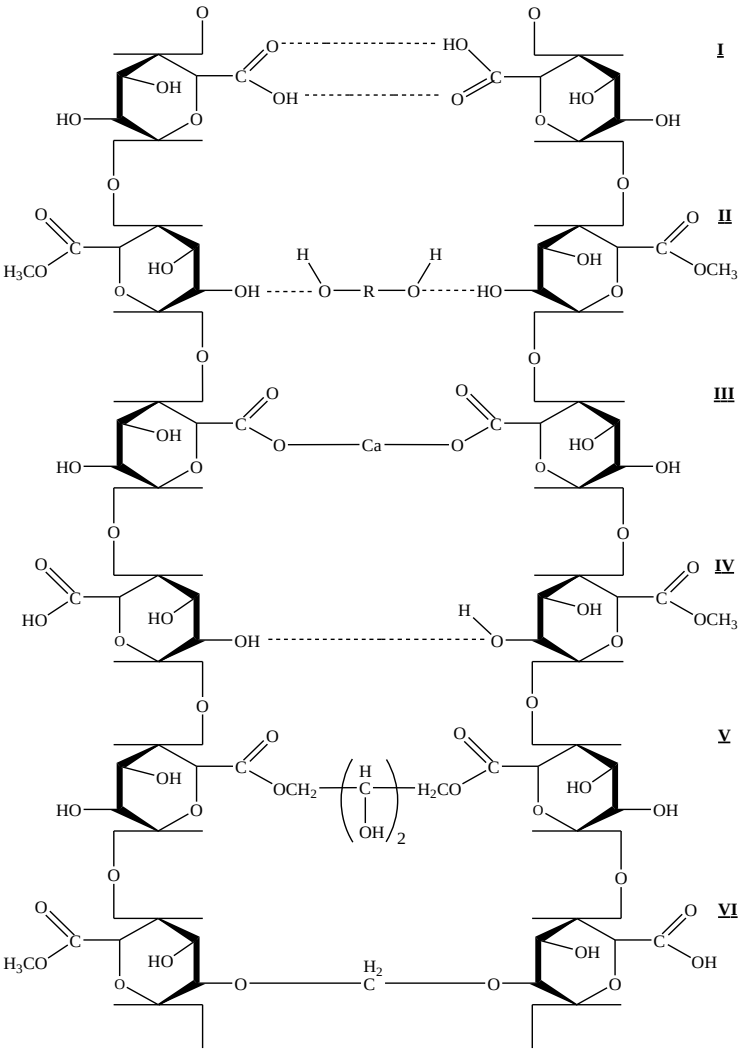

Figure 2.5 - Model of protopectin with different types of links between pectin chains

The nature of beet pectin and the conditions of its extraction do not allow to use it as a structurant and, first of all, for gelation in

the pectin-sugar-acid system. However, the presence in the pectin molecule of ferulic acid residues allows to obtain gels by peroxidase crosslinking with peroxidase and hydrogen peroxide. The content of ferulic groups in beet pectin can range from 0.15% to 0.7%, which depends primarily on the state of raw materials and extraction parameters [88].

Extraction of pectin substances from biochemically prepared raw materials involves the creation of hydrolysis conditions that achieve optimal yield of the target product and the corresponding analytical characteristics and, in particular, the content of ferulic groups in pectin.

2.7.1 The influence of technological parameters of the hydrolysis process of beet raw materials protopectin on the content of ferrule groups in the pectin molecule

Comparative studies have been conducted to determine the effect of the physical state of beet raw materials and the conditions of its hydrolysis on the content of ferulic groups in pectin. Dry pulp and fresh sugar beet roots were studied. 3 experiments were performed to obtain pectin samples.

1. Dry pulp after washing with water and swelling in water was hydrolyzed with a solution of hydrochloric acid at pH 0.8...1.0 at a temperature of 75 °C for 2 hours.

2. Dry pulp after washing and swelling in an acidified to pH = 2.2...2.6 environment was hydrolyzed with a solution of hydrochloric acid at pH = 1.2...1.3 at a temperature of 75 °C for 2 hours.

3. Sugar was utilized from chips of fresh sugar beet roots by the method of purposeful fermentation by alcoholic yeast culture. Pectin was removed from sugar-free washed chips. Conditions of hydrolysis with hydrochloric acid solution: pH = 1.3...1.5, temperature 75 °C, duration - 1.5 hours.

Subsequent operations of extraction, purification of pectin extract and precipitation and drying of pectin were performed under the same conditions.

The results of studies on the yield of pectin, galacturonic acid content, methoxyl and ferulic groups and molecular weight are shown in table 2.8.

Table 2.8 - **Pectin yield, content of galacturonic acid, methoxyl and ferulic groups, molecular weight of pectins**

Indicators	1 method	2 method	3 method
Pectin yield, %	15,7	15,2	13,5
The content of galacturonic acid, %	84,2	83,7	83,3
The content of methoxyl groups,%	7,1	8,7	10,6
The content of ferulic groups,%	0,22	0,31	0,47
Molecular weight	31100	41340	57210

According to the obtained data, the yield of pectin and the content of polygalacturonic acid are the highest from dry pulp during hydrolysis in "harsh" conditions, but the methoxyl component, molecular weight and content of ferulic groups are the lowest. Reducing the concentration of hydrogen ions in the hydrolysis medium avoids the deep destruction of the beet pectin molecule.

The side araban and galactan chains are esterified with the remains of ferulic groups, and branching takes place in the areas of galacturonan with rhamnose inclusions. It is known that the destruction of the molecule of beet pectin in acid-thermal hydrolysis primarily occurs at the junction of rhamnosyl residues, resulting in a significant part of the side chains is cleaved from the pectin molecule. Therefore, the content of ferulic groups increases if the hydrolytic cleavage of protopectin is carried out in a medium with a lower concentration of hydrogen ions. Thus, pre-acidification of raw materials allows to increase the pH of hydrolysis by 0.2 ... 0.5 units

compared to the pH of hydrolysis of unprepared pulp, which ultimately leads to an increase in molecular weight, content of methoxyl and ferulic groups.

The use of fresh raw sugar-free beet raw materials allows to obtain pectin with the best analytical characteristics. In the pectin extracted from such raw materials, the content of ferulic groups was 0.47%, which made it possible to obtain a strong gel in the pectin-peroxidase-hydrogen peroxide system at a concentration of the latter of 1.0%.

To establish the optimal modes of hydrolysis of protopectin of fermented beet raw materials for the yield of pectin and the content of ferrule groups in it, a complete factorial experiment was performed, which resulted in mathematical dependences.

2.7.2 Investigation of the hydrolysis process of fermented beet raw materials protopectin

Hydrolysis of protopectin is an internal process and is determined by three main factors: temperature (t), process duration (τ) and hydrogen ion concentration of the hydrolysis medium (pH) [27].

A full factorial experiment was used to quantify the effect of these three parameters on hydrolysis [71, 72]. To do this, we chose a rotatable plan of the central composition. Based on previous laboratory studies on the hydrolysis of biochemically prepared beet raw materials (p.2.4) were determined the zero point of the experiment, the upper and lower levels of variation of independent factors, as well as their values in the "star points" (Table 2.9).

Table 2.9 - **Variation of independent parameters**

Parameters	pH	Temperature (t), °C	Duration (τ), min
-α	1,2	60	50

-1	1,321	66,075	64,175
0	1,5	75	75
+1	1,679	83,925	100,825
+α	1,8	90	120

To obtain a rotatable matrix of the experiment, a series of experiments on the extraction of pectin from biochemically prepared raw materials were performed, which resulted in data on the yield of pectin and the content of ferulic groups in it.

The matrix of the rotatable plan of the second order and the experimental values of yield and content of ferrule groups are given in table 2.10.

The number of experiments in the plan N = 20, the number of repetitions of experiments M = 3, the number of experiments in the center of the plan N_0=6.

Table 2.10 - **Matrix rotatable plan of the second order and experimental values of yield and content of ferrule groups**

№	Yield, %	The content of ferulic groups, %	Coded values			Experimental values		
			x_1 (pH)	x_2 (t,°C)	x_3 (τ,min)	pH	t, °C	τ, min
1	2	3	4	5	6	7	8	9
1	13,06	0,44	0	0	0	1,5	75	85
2	13,95	0,44	0	0	0	1,5	75	85
3	12,99	0,46	0	0	0	1,5	75	85
4	14,12	0,44	0	0	0	1,5	75	85
5	14,01	0,43	0	0	0	1,5	75	85
6	13,15	0,45	0	0	0	1,5	75	85
7	13,01	0,46	1	1	1	1,679	83,925	100,825
8	12,53	0,47	1	1	-1	1,679	83,925	64,175
9	11,07	0,47	1	-1	1	1,679	66,075	100,825
10	10,12	0,48	1	-1	-1	1,679	66,07	64,175

							5	
11	14,89	0,32	-1	1	1	1,321	83,925	100,825
12	13,76	0,34	-1	1	-1	1,321	83,925	64,175
13	13,00	0.37	-1	-1	1	1,321	66,075	100,825
14	12,07	0,37	-1	-1	-1	1,321	66,075	64,175
15	10,74	0,53	α	0	0	1,8	75	85
16	15,30	0,32	-α	0	0	1,2	75	85
17	14,32	0,45	0	α	0	1,5	90	85
18	12,97	0,43	0	-α	0	1,5	60	85
19	13,88	0,42	0	0	α	1,5	75	120
20	11,96	0,42	0	0	-α	1,5	75	50

Calculations of coefficients of regression equations and their statistical estimation of significance, reproduction variances, adequacy of mathematical model were carried out with the help of MathCad Professional software package.

As a result of processing the experimental data, mathematical models for the yield ($\mathbf{Y_1}$) and content of ferrule groups were obtained ($\mathbf{Y_2}$):

$$\mathbf{Y_1=13,69-0,99x_1+0,83x_2+0,58x_3+0,24x_1x_2+0,07x_1x_3+0,11x_2x_3-0,33x_1^2-0,11x_2^2-0,37x_3^2} \quad (2.1)$$

$$\mathbf{Y_2=0,44+0,06x_1-0,01x_2-0,003x_3+0,007x_1x_2-0,002x_2x_3-0,01x_1^2-0,004x_2^2-0,012x_3^2} \quad (2.2)$$

The significance of the coefficients of the equation was evaluated according to the Student's criterion. T_{St} =2,57 at α = 0.05 and the degree of freedom $f_v=N_0-1=5$ [143].

The coefficients of the same name, namely B_{13}, B_{23}, B_{22}, were insignificant for the regression equations of yield and content of ferulic groups.

After excluding insignificant coefficients, the equations became simplified:

$$\mathbf{Y_1=13,69-0,99\cdot x_1+0,83x_2+0,58x_3+0,24x_1x_2-0,33x_1^2-0,37x_3^2,} \quad (2.3)$$

$$\mathbf{Y_2=0,44+0,061x_1-0,01486x_2-0,00293x_3+0,0075x_1x_2-0,01\cdot x_1^2-0,01189x_3^2} \quad (2.4)$$

Checking the adequacy of the equations according to Fisher's test showed that Fisher's calculation criteria F_p are less than the tabular F_t. The tabular value of F_t. = 4.82 at $\alpha = 0.05$ $f_v = N_0-1 = 5$, $f_{ad}=(N-L)-f_{vд}=5$ [145]. Thus, the equations are adequate.

After converting the equations to the natural form, where the parameters are expressed in dimensional quantities, they took the following form:

$$\mathbf{Y_1=-5,13+9,10\cdot(pH)-0,11\cdot(t)+0,41\cdot(\tau)+0,13\cdot(pH)\cdot(t)-7,63\cdot(pH)^2-2,58\cdot10^{-3}\cdot(\tau)^2,} \quad (2.5)$$

$$\mathbf{Y_2=0,46+0,12(pH)-6,81\cdot10^{-3}(t)-1,15\cdot10^{-2}(\tau)+4,04\cdot10^{-3}(pH)(t)-0,23(pH)^2-8,40\cdot10^{-3}(\tau)^2} \quad (2.6)$$

Table 2.11 shows the experimental and calculated data on the derived mathematical models of the yield and content of ferulic groups in pectin

Table 2.11 - **Experimental and calculated data on the yield and content of ferulic groups in pectin**

№	Yield, %		The content of ferulic groups,%	
	experiment	calculation	experiment	calculation

1	2	3	4	5
1	12,07	12,888	0,37	0,376
2	10,12	10,292	0,48	0,483
3	13,76	13,843	0,34	0.351
4	12,53	12,218	0,47	0,488
5	13,0	13,683	0,37	0,37
6	11,07	11,358	0,47	0,477
7	14,89	15,089	0,32	0,345
8	14,18	13,733	0,46	0,483
9	15,3	14,42	0,32	0,313
10	10,74	11,097	0,53	0,518
11	12.97	11,984	0,43	0,452
12	14,32	14,785	0,45	0,436
13	11,96	11,687	0,42	0,415
14	13,88	13,63	0,42	0,405
15	14,05	13,693	0,44	0,444
16	13,95	13,693	0,46	0,444

Graphical representation of the model was built in the form of level lines with two variables and one fixed (center of the plan) values of factors. Figures 2.6 and 2.7 show the lines of pectin yield

and the content of ferrule groups in the coordinates (τ - t) at pH = 1.55.

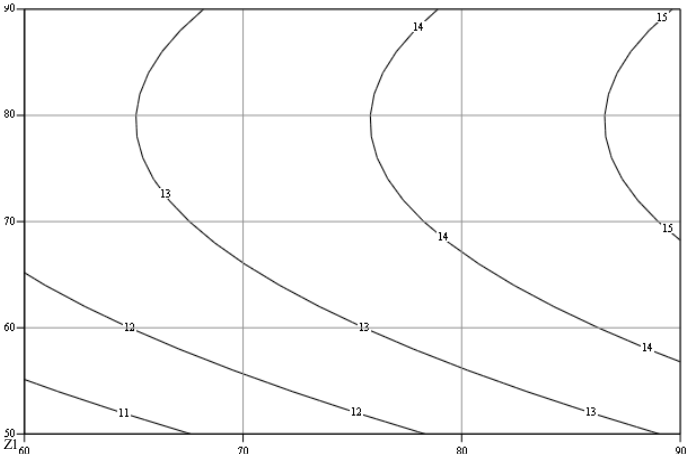

Figure 2.6 - Lines of the yield level in the coordinates τ - t at pH = 1.55

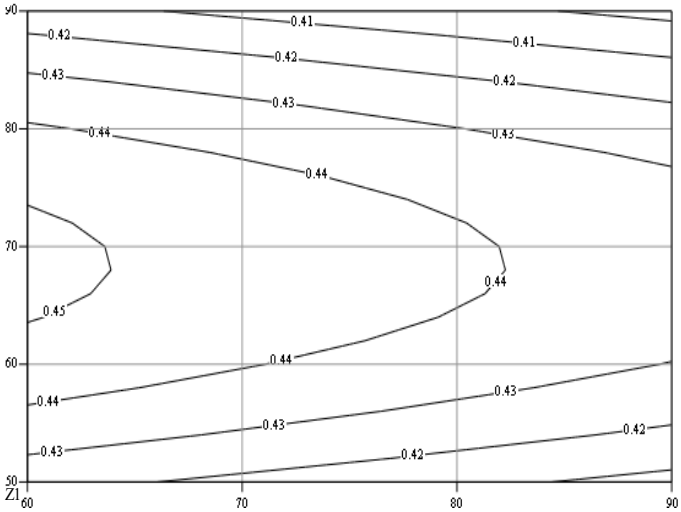

Figure 2.7 - Lines of the level of ferulic groups in the coordinates τ - t at pH = 1.55

Analysis of the model shows that the greatest effect on both the yield and the content of ferrule groups has the pH level of the medium. But lowering the pH, as indicated by the negative value of the coefficient in equation (2.3), leads to an increase in yield. A positive value at x1 in equation (2.4) indicates that the content of ferulic groups in the pectin molecule increases with increasing pH of hydrolysis. The temperature factor and duration have much less effect. Rising temperatures and increasing the duration of the process have a positive effect on the yield of pectin, but negatively - on the content of ferulic groups.

To determine the optimal conditions for hydrolysis, it is advisable to make calculations to optimize the process.

2.7.3 Optimization of the hydrolysis process of fermented beet raw materials protopectin

In order to establish the optimal technological parameters of the process of hydrolysis of the protopectin of fermented beet raw materials, the obtained experimental data were optimized. With the help of one initial parameter it is impossible to unambiguously characterize the researched process, therefore the generalized optimization criterion which allows to generalize the chosen local criteria of optimality by the only quantitative indicator was chosen for the decision of optimization problem. [144, 145, 146]:

$$F = \prod_{i=1}^{n} f_i^{'}(x)^{\lambda i} \rightarrow \max \qquad (2.7)$$

де $f'_i(x)$ - local criteria of optimality in dimensionless form; λ_i – weight coefficients, i=1…5.

The following local criteria (in kind) were chosen to evaluate the efficiency of the hydrolysis process.:

$f_1(x)$ – pectin yield, %;

$f_2(x)$ – the content of ferulic groups in pectin,%;

$f_3(x)$– pH of hydrolysis;

For $f_1(x)$ and $f_2(x)$ mathematical models in natural form (equations 2.5 and 2.6) are established, which adequately express the dependence of the initial process parameters on the input factors

Weight coefficients $\lambda_1=\lambda_2=0{,}45$ for $f_1(x)$ and $f_2(x)$, $\lambda_3=0{,}1$ for $f_3(x)$.

The use of the generalized optimization criterion requires the transformation of local optimality criteria from natural to dimensionless form, which is carried out by the Harrington method through the determination of intermediate parameters fb_i using the

desirability function. New dimensionless values of local criteria obtained using the desirability function vary from 0.01 to 0.99 due to the insensitivity of their values when approaching 0 or 1.

The interval 0.01… 0.99 is divided into five parts to better reflect the criteria. The interval from 0.01 to 0.2 corresponds to the concept of "very bad", from 0.2 to 0.37 - "bad", from 0.37 to 0.63 - "satisfactory", from 0.63 to 0.8 - "good", from 0.8 to 0.99 - "very good".

The program for converting the natural values of local optimality criteria into dimensionless form by the Harrington method, as well as the program for optimization and calculation of optimal parameters of the hydrolysis process were performed using the Mathcad Professional software package.

Figure 2.8 shows the response surface of the generalized criterion, Figure 2.9 shows the level lines of the generalized optimality criterion.

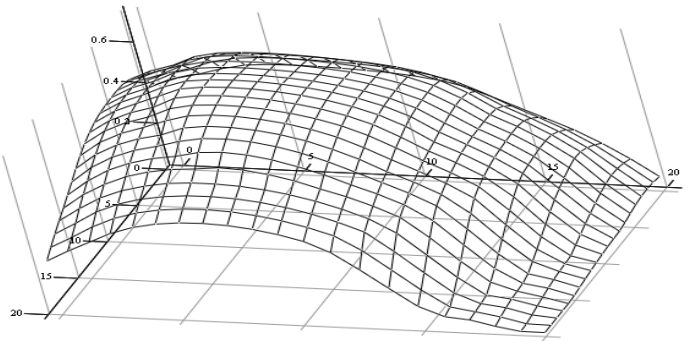

Figure 2.8 - Response surface of the generalized optimality criterion

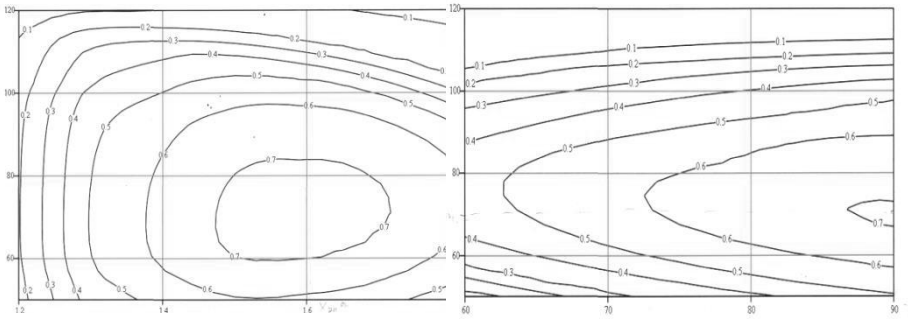

Figure 2.9 - Level lines of the generalized optimality criterion

Thus, using the obtained equations, using the generalized criterion of optimality, the values of the optimal technological parameters of the process of hydrolysis of the protopectin of fermented beet raw materials were determined. Such hydrolysis parameters are pH = 1.47, temperature 84 ° C, duration 71 minutes

However, the established regimes do not allow to achieve high degrees of extraction of pectin. A significant number of them remain in the raw material due to incomplete hydrolytic cleavage, as well as as a result of the reverse reaction.

2.8 Features of a continuous method of extracting pectin from beet raw materials

The efficiency of hydrolytic cleavage of protopectin is evaluated by the yield of water-soluble pectin, the content of polygalacturonic acid, analytical characteristics, the amount of ballast substances that determine the functional properties of pectin. The requirements of modern production, which are based on the principles of environmental friendliness, energy and resource saving, include the improvement of appropriate technological regimes and equipment design for efficient hydrolysis.

Harsh conditions of hydrolysis of beet raw materials lead to the destruction of the polymer complex of protopectin, much of which is formed from chains connected by calcium and magnesium bridges [16]. During the destruction of polymer conglomerates during hydrolysis, calcium and magnesium ions are released and their concentration in the medium increases, which, in turn, accelerates the backlash. Removal of metal ions from the hydrolysis medium prevents inhibition of the direct reaction. Researchers suggest different ways to intensify the process of hydrolysis and extraction of metal ions from the reaction medium.

Krasnodar scientists have developed a two-stage hydrolysis of swollen beet pulp. The first stage involves harsh conditions of hydrolysis at a mass ratio of swollen pulp and hydrolyzing solution of 0.7 (pH = 1.0… 1.2, t = 75 ° C, τ = 0.6 h) and separation of pectin extract. In the second stage, the hydrolysis is continued by adding a solution of hydrochloric acid, at a weight ratio of 0.62 (pH=1.0…1.2, t =75°C, τ = 0.9 h) [20].

In the method developed by NUHT scientists for the derivation of inhibitory factors of hydrolytic cleavage of protopectin is due to the introduction into the hydrolysis mixture of the disodium salt of ethylenediaminetetraacetic acid (Trilon B). Trilon B is characterized by higher complexing activity in comparison with pectin, so its introduction into the hydrolysis medium disturbs the balance in the system "pectin - metal ions". As a result, hydrolysis in the presence of Trilon B produces more pectinic acid, which increases the yield of the finished product, increases the purity and complexing ability of pectin [109].

Researches by Karpovich MS etc. it is proved that the mass ratio of solid: liquid does not affect the degree of hydrolysis. The expediency of hydrolysis in boiling conditions under vacuum with subsequent extraction of pectin substances is substantiated in the

works [9, 20]. The process of hydrolysis-extraction of raw beets is carried out in four stages, which consist of:

Step 1 - keeping the prepared pulp in a solution of acid reagent at pH = 1.85...2.0, t = 75 ... 80 °C for 1 hour;

Stage 2 - connection of vacuum, holding at a residual pressure of 85 kPa until the pH of the hydrolysis mixture is 1.2...1.5 and reducing ratio of masses pulp:liquid phase from 0.08 (1:12) to 0.12 (1: 8.5);

Stage 3 - disconnection from the vacuum and thermostating of the hydrolysis mixture for 1.3 hours at t = 75 ... 80 °C;

Step 4 - adding water to the apparatus and extraction for 0.5...0.7 hours with periodic stirring. All operations are performed in one hydrolyzer.

In order to improve the hydrolysis process, taking into account the scientific and practical achievements of the above researchers, developed a method of continuous extraction of pectin to obtain in one technological cycle of different types of pectins with excellent functional properties [101].

According to the method of continuous hydrolysis-extraction of pectin, the process consists of successive stages, at each of which it is possible to set the desired modes of the technological cycle. Thus, to obtain two types of pectin it is necessary to carry out two-stage hydrolysis: in the first stage it is necessary to establish a "soft" hydrolysis regime, separate part of the pectin extract and obtain pectin with a high content of feruloester groups, and in the second stage to set "hard" hydrolysis conditions for deep destruction of the protopectin complex and to obtain low-esterified pectin with high complexing ability. This differential approach allows to extract pectin substances in the amount of 70…75% of their content in the raw material.

To obtain highly purified pectin, it is necessary to carry out a two-stage hydrolysis, the second stage of which involves the introduction of Trilon B in the hydrolysis mass.

In order to implement the developed method, an installation for a continuous hydrolysis process is proposed (Fig. 2.10).

The installation includes a battery of devices 1, 2, 3, 4, which are connected in series by pipeline 8 with heat exchangers such as "pipe in pipe" 5, 6, 7. Each of the devices is a vertical cylindrical steel enameled housing 10 with jacket 11 and with mixing device 9 on the shaft 12 with drive 13. Trigger holes: 14 for hydrolysis mass, 15 for condensate [102].

The process of hydrolysis to obtain two types of pectins is as follows. Prepared beet raw material and hydrolytic factor in a mass ratio of 1:1 are fed into the apparatus 1. The mixing device 9 provides efficient mass transfer in the hydrolysis system. As the apparatus 1 is filled, the hydrolysis mixture is moved through the lower drain hole 14 and the pipe with the heat exchanger 5 to the upper part of the next apparatus 2 and maintained at pH 1.4...1.5, temperature 75...80 °C for 45…50 min. After the first stage of hydrolysis, from the hydrolysis mass through the lower fitting equipped with a sieve, the pectin extract is drained and the hydrolysis mass is sent through the heat exchanger 6 to the apparatus 3.

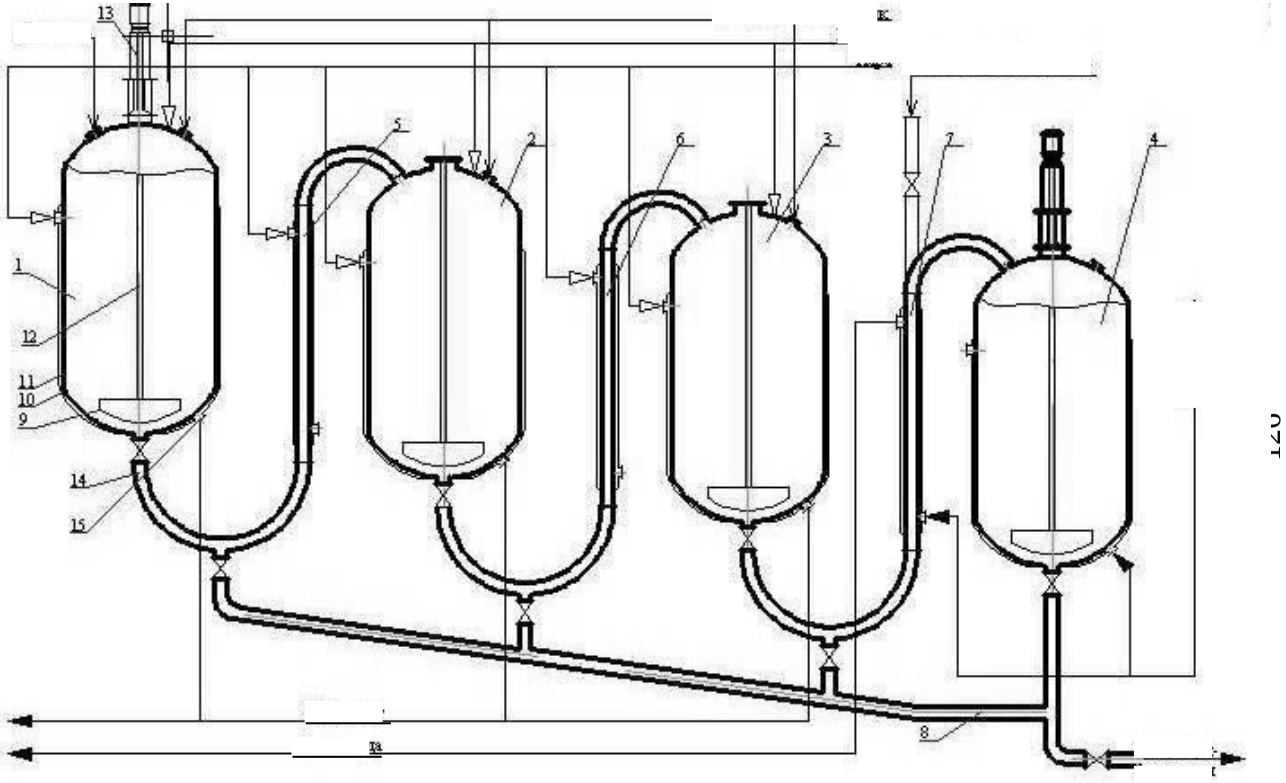

Figure 2.10 - Installation for a continuous process of pectin hydrolysis

In the apparatus 3 add an acid solution, create a vacuum and the hydrolysis mass is maintained at a mass ratio (dry matter: liquid) of 0.12 (1: 8.5), pH = 1.1…1.2, at a temperature of 70...75 °C for 40…45 minutes. Thinning saves 45...55% of hydrolytic factor and neutralizing reagents. After the apparatus 3, the hydrolyzed mixture is cooled in the heat exchanger 7 to a temperature of 30...40 °C for extraction. Adding water twice the amount of raw material in the extractor apparatus 4 increases the pH of the medium to 1.7...1.9, and soluble pectin diffuses into the liquid phase without significant losses due to acid-thermal degradation. If it is necessary to neutralize or obtain modified pectins in the apparatus 4, it can be added the appropriate reagents (NaOH, NH_4OH). Placing the devices on the descending makes it possible to unload individual devices by gravity, as well as wash them.

Obtaining highly purified pectin (HPP) is carried out as follows. The supply of raw materials, reagents, mixing, heating and mass movement are similar to the previously described process. In apparatus 2 under vacuum, moisture is removed and hydrogen ions are concentrated in the hydrolysis mixture (pH decreases from 1.5...1.7 to 1.2…1.3 and the phase ratio from 0.08 to 0.12). After keeping at a temperature of 70...75 °C for 40…45 minutes the hydrolysis mass is sent through the heat exchanger 6 to the apparatus 3, where the solution of Trilon B is added at the rate of 0.01…0.03% by weight of the hydrolysis mixture. In the apparatus 3, the hydrolysis mass is maintained at a temperature of 70...75 °C and pH = 1.4…1.5 for 30…40 minutes. Subsequent cooling and extraction operations are performed in the same way as in the first process.

According to the developed method, studies on continuous hydrolysis-extraction with subsequent isolation of pectin from beet raw materials. The obtained dry pectin was analyzed by yield to dry air mass of raw materials, quality indicators and metals content. As a

control, a sample of beet pectin obtained from the same raw material without the use of two-stage hydrolysis and addition of Trilon B. The results are given in table. 2.12.

Table 2.12 - **Yield, analytical characteristics of beet pectin and its metals content**

Indicator	Value for pectin			
	Control	With intermediate extract separation		HPP
		Type 1	Type 2	
Yeild,%	11,0	6,2	7,7	15,2
The content of polygalacturonic acid, %	62,1	51,0	65,6	72,0
The content of methoxyl groups, %	7,2	8,0	7.6	8,1
Degree of esterification, %	37	53	42	56
Molecular weight	47000	51700	45800	51000
Complexing ability, mg Pb^{2+}/mg	240,0	316,0	308,0	360,0
The content of feruloether groups,%	0,3	0,56	0,25	0,2
Metals content, %:				
Ca^{2+}	$3{,}4 \cdot 10^{-1}$	$2 \cdot 10^{-1}$	$7 \cdot 10^{-2}$	$4 \cdot 10^{-2}$
Mg^{2+}	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	$2 \cdot 10^{-4}$
Fe^{2+}	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$3 \cdot 10^{-3}$	$4 \cdot 10^{-4}$
Cu^{2+}	$3{,}6 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-5}$
Pb^{2+}	$6{,}7 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$2 \cdot 10^{-5}$
Zn^{2+}	$3{,}7 \cdot 10^{-2}$	$3{,}5 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$1 \cdot 10^{-3}$
Cd^{2+}	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	–
Σ	0,4275	0,2842	0,1062	0,041

The developed method and equipment allow to obtain the target product with high yield and quality performance at lower consumption of chemical reagents, which, in turn, affects not only the cost of pectin, but significantly improves the environmental conditions of production.

2.9 Obtaining cross-linked pectins and their rheological properties

Pectin is characterized by reactions with di- and polyfunctional compounds that can crosslink pectin molecules into three-dimensional network structures through linear regions, forming water-soluble, stable, thermo-irreversible gels bound by major valences.

Pectic substances can give derivatives, which are obtained from the interaction of secondary hydroxyl and carboxyl groups. Crosslinking of pectins with formaldehyde (in the presence of hydrochloric acid as a catalyst) is quite easy due to the transplacement of hydroxyl groups in the second and third carbon atoms. Crosslinking between two carboxyl groups of pectin chains is possible when interacting with erythrodioxide or mustard gas [80].

Crosslinking causes the formation of modified forms of pectin and changes in its structural and mechanical properties.

We have studied the cross-linking of beet pectin with the enzyme peroxidase and hydrogen peroxide according to the reaction, which is characterized by the interaction of ferulic acid residues in branched fragments of the pectin molecule.

Samples of beet pectin were obtained from fresh sugar beet roots, sugar removal of which was carried out by targeted fermentation with a culture of alcoholic yeast. The peroxide-peroxidase crosslinking reaction was performed in solutions with a mass fraction of pectin of 1.0; 1.5 and 2.0%.

To study the ability of polysaccharides to gelation, the method of physicochemical mechanics can be used, which studies the dependence of the structure, mechanical properties of dispersed systems and macromolecular compounds on physicochemical processes occurring in volume and at the phase interface [87]. It establishes the dependence of the mechanical properties of the system on its chemical composition, structure, physicochemical

factors, studies the mechanism of deformation, flow and destruction of bodies [82].

According to the results of experimental data, rheological flow curves $D_r = f(\tau_r)$ were constructed, which represent the dependence of the strain rate on shear stress, and rheological curves of effective viscosity $\eta = f(\tau_r)$, ie the dependence of viscosity on shear stress in conditions of stationary, stable and laminar flow. Such curves for aqueous solutions and gels of crosslinked (cr) and uncrosslinked (uncr) pectin at concentrations of 1%, 1.5% and 2% are presented in Fig. 2.11 and Fig. 2.12.

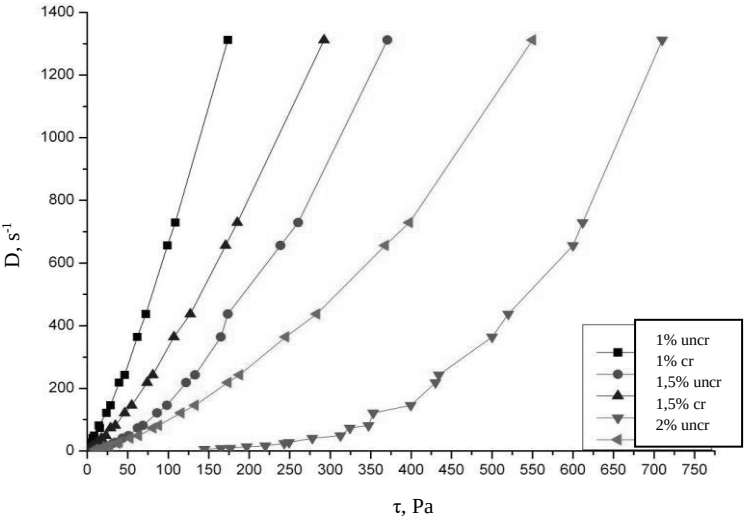

Figure 2.11 - Dependence of the rate of deformation of beet pectin solutions on the shear stress

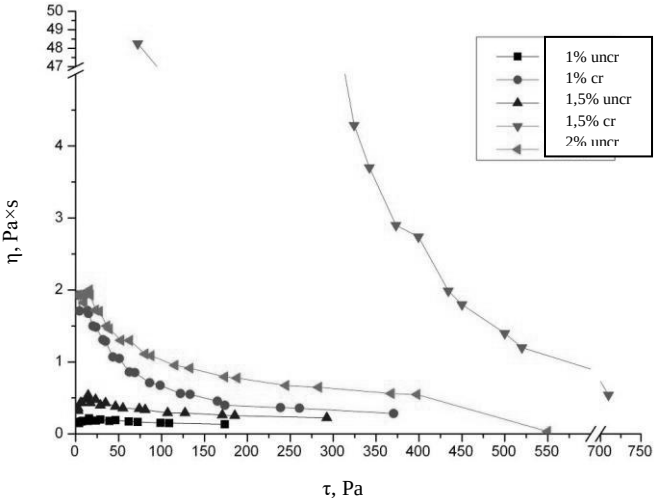

Figure 2.12 - Rheological viscosity curves $\eta=f(\tau_r)$ of pectin solutions of different concentrations

Based on these dependences, the rheological characteristics of the strength and viscosity of the obtained solutions were determined, namely:

- P_{K1} – conditional static limit of the ability to flow, directly measured on the device at the initial moment of deformation;
- P_{K2} – conditional dynamic limit of the ability to flow;
- P_m – upper limit of the ability to flow or strength limit, above which the flow of the system with constant viscosity is observed. The value of P_m is also called the voltage of the practically destroyed structure;
- η_0 – the highest viscosity at shear stress, equal to the conditional static yield strength;
- η_m – the lowest effective viscosity, ie the viscosity of the practically destroyed structure;

- (η_0–η_m) – the magnitude of the viscosity anomaly, which characterizes the change in the strength of the structure during deformation.

The obtained data are shown in table 2.13.

Table 2.13 - **Rheological characteristics of pectin solutions**

Sample of pectin solution	P_{K1}	P_{K2}	P_m	η_m	η_0	η_0-η_m
	Pa			Pa·s		
1% uncross-linked	0	2,5	6,5	0,013	0,022	0,009
1% cross-linked	2,90	9,2	19,1	0,030	0,190	0,16
1,5% uncross-linked	0	5,0	12,1	0,022	0,054	0,032
1,5% cross-linked	7,2	34,1	45,8	0,05	4,80	4,75
2% uncross-linked	0,3	15,3	36,5	0,04	0,20	0,16

According to the rheological flow curves, aqueous solutions of uncross-linkedpectin with concentrations of 1.0% and 1.5% in accordance with the generally accepted classification in rheology are structured liquids, because they have the value of P_{K1}=0. A solution of uncross-linked pectin with a concentration of 2.0% and solutions and gels of crosslinked pectin with concentrations of 1.0% and 1.5% are solids, because they have a value of P_{K1}>0. To start the flow of such systems, it is necessary to apply some shear stress that is different from zero. Therefore, the pectin crosslinking process changes the type of rheological system formed by pectin gels from a structured fluid to a solid, even at relatively low pectin concentrations of the order of 1.0%.

Rheological studies have shown (Fig. 2.12) that all samples of pectin gels, but to varying degrees, have a viscosity anomaly, ie a decrease in effective viscosity with increasing shear stress. The phenomenon of reducing the viscosity anomaly of polymer systems has been observed by many authors, in particular [82]. As noted in the literature, the cause of the viscosity anomaly is the orientation of macromolecules in the flow (the degree of orientation increases with increasing velocity gradient) or - even more - the destruction of the

spatial structure formed in solutions of macromolecular compounds. The viscosity anomaly appears to be most pronounced in 1.5% crosslinked pectin gels.

As evidenced by the results presented in table. 2.13, crosslinking significantly intensifies the processes of structure formation in solutions and gels of pectin, most noticeable in gels with 1.5% concentration of pectin. If crosslinking in solutions of 1.0% pectin leads to an increase in their strength $P_{K1,}$ P_{K2} and P_m approximately 3.0 - 3.5 times, and viscosity anomalies - an order of magnitude, then increasing the concentration of pectin to 1.5% there is a sharp increase in strength (almost 7 times), and the magnitude of the viscosity anomaly increases by two orders of magnitude. The rheological parameters of 1.5% crosslinked pectin gels are much higher than those of crosslinked pectin with 2.0% concentration.

Thus, the reaction of peroxide-peroxidase crosslinking of beet pectin allows to repeatedly strengthen the processes of structure formation in aqueous solutions of pectin with low concentrations.

2.10 Technological scheme of pectin production from biochemically treated raw materials

The results of research of biochemical preparation of beet raw materials and extraction of pectin from it allowed to develop the technology of pectin and pectin products with specified properties, to provide a complex use of plant raw materials in the production of pectin products. A process-hardware scheme for the production of beet pectin and pectin products (Figs. 2.13, 2.14) has been developed [103, 104, 105, 106, 107, 109].

Preparation of raw materials. The main raw materials for pectin production using the proposed technology are fodder and sugar beets, as well as other roots, which contain a sufficient amount of pectin and fermented sugars.

Root crops are delivered to the enterprise from fields or kagats intended for long-term storage. Storage, transportation and unloading of root crops is carried out under the conditions of preventing them from rot and injury. Batches of raw materials with rotten roots are not allowed for processing.

The mass of roots contains foreign plant and mineral impurities. The surface of root crops contains residual amount of soil, and also the connected beet. For cleaning of root crops from extraneous and free and connected impurity process of their washing is provided.

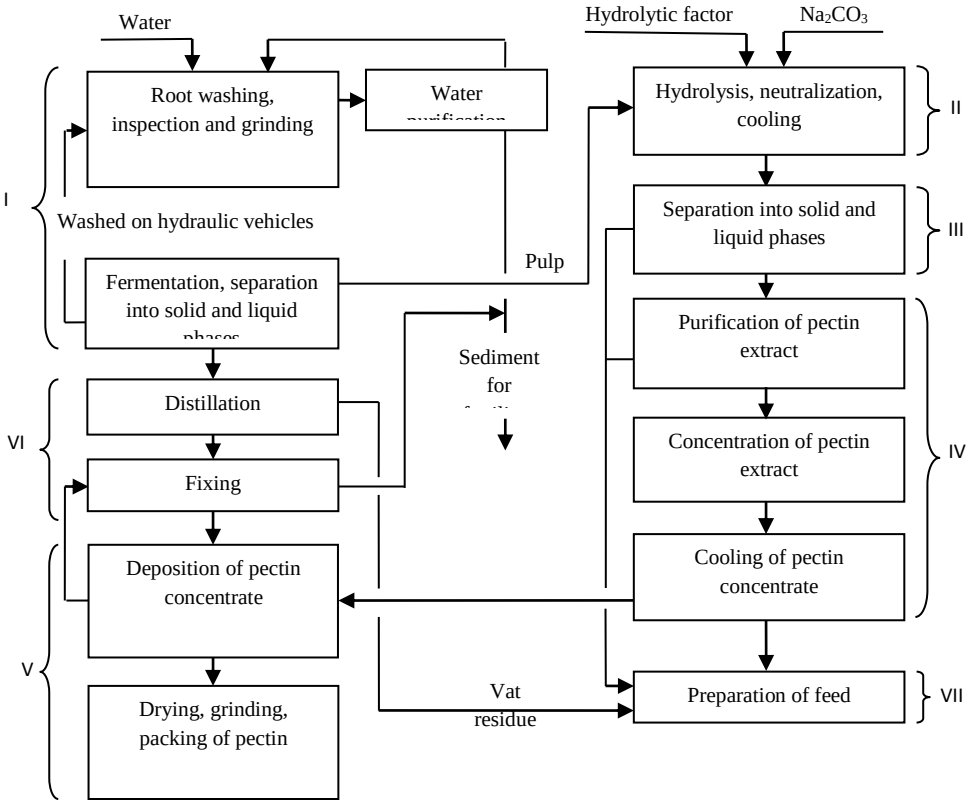

Figure 2.13 - Block diagram of beet pectin production

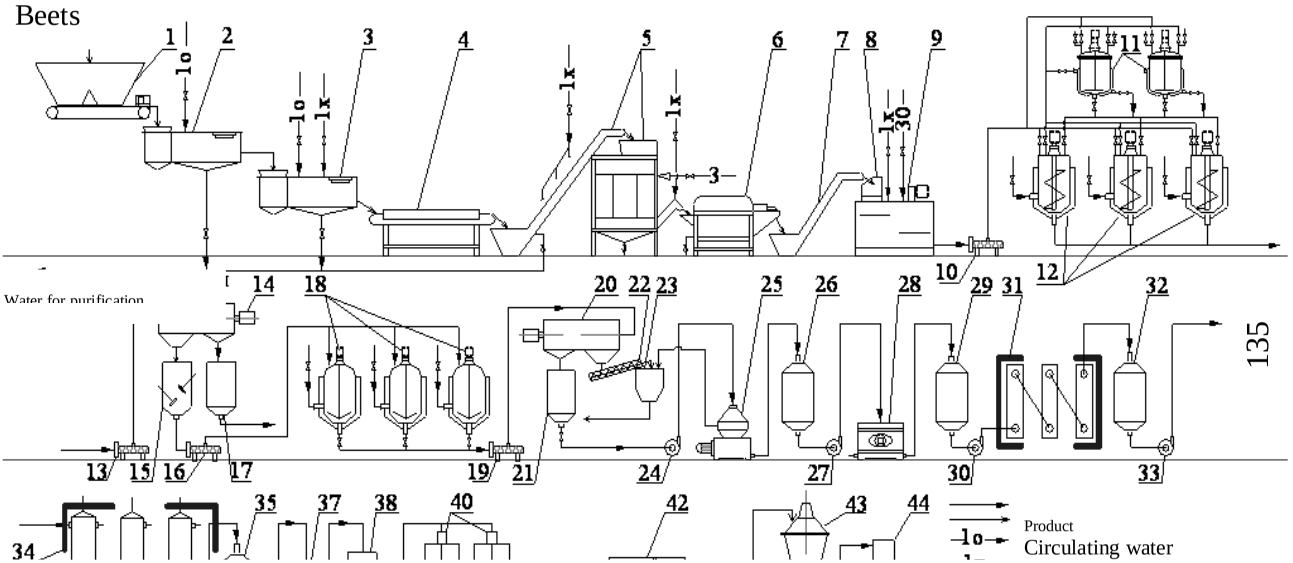

Figure 2.14- Apparatus-technological scheme of pectin production from sugar beet roots

1 - hopper scales; 2,3 - drum washing machine; 4 - inspection conveyor; 5 - steam-thermal unit; 6 - washing machine; 7 - elevator; 8 - crusher; 9 - tank for the pulp; 10, 13, 16, 19, 41 - screw pump; 11 - yeast generators; 12 - fermentation apparatus; 14, 20 - decanter; 15 container for pulp; 17 - capacity for yeast suspension; 18 - hydrolyzers; 21 - tank of pectin extract; 22 - conveyor; 23 - tank for unpent pulp; 24, 27, 30, 33, 36, 39 - centrifugal pump; 25 - centrifuge; 26, 29, 32, 35, 38 - tanks; 28 - diatomaceous earth filter; 31 - ultrafiltration unit; 34 - evaporator installation; 37 - heat exchanger; 40 - coagulator; 42 - Bucher press; 43 - rotary dryer; 44 - alcohol trap.

Weighed beets from the hopper scales (pos. 1) are fed for washing, which takes place in 2 stages on drum washing machines (pos. 2,3), the first uses circulating water, the second - circulating and clean. The beet roots are washed from the dirt.

The cleaned and washed roots are carefully checked on the inspection conveyor (pos. 4), from which by the elevator with shower rinsing is fed to the steam-thermal unit (pos. 5). In this unit, whole roots are subjected to heat treatment under pressure. This operation is intended for purification by removing the top layer of root crops in order to neutralize the microflora, which can lead to unintended loss of sugars during fermentation. The final washing of the roots takes place in the washing machine (pos. 6). It is a bath with a double bottom, along the bath is a rotating shaft with blades. The bath is filled with running water. Located along the helical line, the blades transfer raw materials, provide good washing and move it forward, unloading at the end of the bath to the elevator (pos. 7).

To create the necessary conditions for washing raw materials in the saving water mode in the washing department provides for the reuse of conveyor-washing water. The precipitated part of the dirt from the collection is sent to fertilize the fields.

From the elevator the roots are fed to the crusher (pos. 8). Beet pulp accumulates and mixes with water in the tank (pos. 9). To exclude the darkening of beet pulp due to oxidation of phenolic compounds in the tank serves a solution of sulfuric acid (H_2SO_3).

The supply of a mixture of beet pulp with water (beet wort) in the fermentation apparatus (pos. 12) is carried out by a screw pump (pos. 10). Water can be used to dilute the beet pulp after washing the fermented raw materials. The temperature of beet wort should be 30 ... 32 °C.

Fermentation of beet pulp. The crushed mixture of root crops with a total sugar content of about 15% is mixed with water in

a ratio of 1: 1 (q = 1). This mass is the original wort for fermentation and is used to produce industrial yeast.

Production yeast is cultivated under aerobic conditions in yeast generators (pos. 11), the volume of which is up to 10% of the volume of the fermentation apparatus. Operations to prepare the mash for fermentation (pasteurization, bringing the reaction medium to the desired pH value, cooling) are carried out in this apparatus.

At establishment of process of cultivation as sowing yeast in the yeast generator use their volume in number of 10% from the previous cycle of cultivation before giving in the fermenting device. Before starting the cultivation of yeast, the yeast generator is washed with hot water, steam sterilized, cooled. Then the mash is collected, pasteurized at a temperature of 85 °C, cooled to 30 °C and sown yeast (8...10% to the volume of the yeast generator) is introduced into the apparatus. The accumulation of yeast biomass lasts 12...18 h at a temperature of 28...30 °C and moderate aeration with air.

The fermentation process is carried out periodically in fermentation apparatus (pos. 12). The mash with a temperature of 28...30 °C is pumped into the fermenter, set in it production yeast in the amount of 10% of the volume of the mash. Fermentation is carried out at a temperature of 28...30 °C for 24...36 hours. In the process of fermentation from the exhaust gases capture alcohol vapors in the alcohol traps. The fermentation medium is cooled through the cooling jacket with return water. Utilization of carbon dioxide released during the fermentation of sugars is possible.

After fermentation, the fermented mass is divided in the field of centrifugal forces on the decanter (pos. 14) into sugar-free beet pulp and alcohol mash. The pulp accumulates in a container with a stirrer (pos. 15), where in order to completely remove the alcohol it is washed. The washed pulp is pumped for hydrolysis by a screw pump (pos. 16). The mash is collected in a container and sent for

distillation and separation of ethyl alcohol. The wash water is used to dilute the raw material.

At the stage of fermentation of raw materials from raw crushed roots there is practically no production waste. Washing water after sanitation of the devices between cycles is sent to treatment plants..

Hydrolysis of beet tissue protopectin. The process of hydrolysis of protopectin is carried out in a hydrolyzer (pos. 18), which is a sealed enameled apparatus equipped with a steam jacket and a stirrer.

The apparatus creates a vacuum and serves water in an amount corresponding to the ratio of pulp: liquid phase 1: 1 (q = 1).

With continuous stirring, the estimated amount of hydrolytic factor (hydrochloric acid solution, etc.) is fed into the apparatus.

After the supply of hydrolytic factor and the establishment of the reaction medium pH = 1.5...1.2 release the vacuum and heat the contents to 80...85 °C. Upon reaching the specified temperature in the apparatus create a vacuum and evaporate some of the water (20...40%) at a boiling point of 75...80 °C.

The duration of the hydrolysis process is 90…150 minutes and is specified in the laboratory by estimating the amount of pectin based on alcohol precipitation in vitro, as well as organoleptic parameters of the hydrolysis mass.

Extraction of pectin. At the end of the hydrolysis process, cold water is poured into the hydrolyzer in an amount that creates a mass ratio of 1: 3 (q = 3) relative to the amount of beet pulp. After stirring, the contents are infused for 30...40 min at atmospheric pressure.

The content of pectin substances in the hydrolysis mass is determined by the reaction medium (pH). If the pH <3.0...3.2, the contents are neutralized with a solution of Na_2CO_3.

After neutralization, the hydrolyzed mass is pumped (pos. 19) to the decanter (pos. 20). Pectin extract accumulates in the tank (pos. 21). Unburned pulp is sent by conveyor (pos. 22) to the tank (pos. 23). Then the pulp is used in the preparation of feed.

Purification of pectin extract. The resulting extract contains suspended plant fiber particles that need to be removed. Purification is carried out by centrifugation followed by filtration.

The pectin extract is fed to the centrifuge (pos. 25) by pump (pos. 24). The separated extract accumulates in the tanks (pos. 26), and then pumped (pos. 27) to the diatomaceous earth filter (pos. 28). Pectin extract, cleaned of suspended impurities, is collected in the tanks (pos. 29).

Concentration of pectin extract. Concentration takes place on an ultrafiltration unit and in a 3-hull vacuum evaporator unit.

The extract is concentrated to a pectin content of 2.0...3.0% in vacuum evaporators at a temperature of 70...78 °C.

Evaporated to a given concentration of pectin concentrate from the storage tank by pump (pos. 36) is sent for cooling in the heat exchanger (pos. 37).

Deposition of pectin sustances and coagulate separation. The technological scheme provides for the extraction of pectin substances from pectin concentrate and their precipitation with ethyl alcohol.

To do this, the pectin concentrate is cooled through a heat exchanger (pos.37) to a temperature not exceeding 15...18 °C and mixed with a triple amount of ethyl alcohol with a strength of not less than 90% vol in the tank (pos. 38), then sent to the coagulator (pos. 40). In the process of precipitation, pectin substances under the action of ethyl alcohol are released from the solution in the form of a precipitate (coagulate).

The pectin-alcohol-water mixture obtained in the coagulator enters the filter (pos. 42), where the spent alcohol is separated, the coagulate is washed and pressed several times.

The pectin precipitate is sent to a rotary dryer (pos. 43) with an alcohol trap (pos. 44), dried to a humidity of 10 ... 12%. The temperature of the drying process of pectin coagulate is not more than 80 ... 85 °C. Dried pectin is crushed and packed. The finished product is packaged using plastic inserts and cardboard boxes.

Pectin is stored in closed ventilated rooms at a relative humidity of not more than 75% and a temperature not exceeding 30 °C.

Obtaining ethyl alcohol - a by-product formed in the preparation of pectin-containing raw materials. Preparation of pectin-containing raw materials from root crops involves the maximum removal of ballast pectin substances, including sugars. The technology involves the extraction of sugars by fermentation to obtain a by-product - ethyl alcohol, which is used in later stages of the process.

Obtaining ethyl alcohol consists of 2 technological processes:

- distillation of the fermented wort, obtained from the liquid phase of the fermented mash (extraction of ethanol from the mash in the vat apparatus);
- fixing of fermented wort condensate and removal of concomitant impurities in the vat distillation apparatus of periodic action.

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3 APPLICATION OF PECTIN AND PECTIN PRODUCTS IN FOOD PRODUCTION

The modern food industry uses a wide range of food additives of various origins to provide food products with the necessary technological, organoleptic, physicochemical and other characteristics and properties.

Pectin is a natural polysaccharide that combines the properties of a structuring agent and a biologically active compound. Structural formation in products with pectin is manifested in the ability to form strong gels, give stability to emulsions, thicken food masses. The biological activity of pectic substances is expressed in detoxifying, radioprotective, antioxidant, hypoglycemic, immunostimulatory effects. This gives grounds for its widespread use in the creation of health products, preventive nutrition and dosage forms.

3.1 Pectin as a biologically active additive

The rapid development of scientific and technological progress not only ensures the well-being of the population, but is a source of harmful factors and toxic substances, heavy metals, radionuclides, pesticides that pollute the environment and enter the human body, causing various diseases, reducing its resistance.

Due to the high scientific level of medical and biological research, the unique properties of pectin have been discovered, which makes it possible to widely use it in the food, pharmaceutical, cosmetic and medical industries.

The main pharmacological properties of pectin include:

Ability to bind toxic metal ions, radionuclides, pesticides. The therapeutic effect of pectin is due to its chemical structure. The polymer chain of polygalacturonic acid, the presence of free chemically active carboxyl groups and alcohol hydroxyl contribute to

the formation of strong insoluble complexes with polyvalent metals, which are then excreted from the body. Pectin has an active complexing ability to radioactive cobalt, strontium, cesium, zirconium, ruthenium, yttrium and other metals [1,2-11].

The duration of complexation of pectin with radionuclides averages 1…2 hours. According to the recommendations of health organizations, the daily requirement for pectin substances for people employed in enterprises with harmful working conditions is 15…16 g/day [3,4].

The ability to lower blood sugar and normalize carbohydrate metabolism. More than three hundred years have passed since the discovery of a disease such as diabetes, which means "losing sugar" in Greek. Glucose is the main source of energy for cells. But it can get into the cell only with insulin. If there is no insulin or it is not produced enough, the blood glucose level rises. The cells of the body at the same time feel energy hunger and begin to use substances unfit for consumption, such as fats. In this case, acetone (so-called ketone bodies, which are products of fat oxidation) appears in the blood and urine. This condition, called ketoacedosis, is very dangerous, as it can lead to death in the future [15].

Research in recent decades has focused on the study of blood glucose lowering with pectin use. The results of studies have shown that with daily consumption of 5 g of pectin with each meal, there is a decrease in glucose. This led to the conclusion that pectin affects blood sugar levels by slowly emptying the esophagus and further absorption occurs due to increased viscosity of the gastrointestinal tract under the influence of pectin [16].

The ability to lower cholesterol. Cholesterol is a lipid that plays an important role in metabolism. In the human body, it performs various physiological functions, including the formation of vitamin D3, bile acids, sex hormones. There are several types of

cholesterol: high-density cholesterol, which has the above functions in the human body, and low-density cholesterol, which, deposited on the walls of blood vessels, creates significant changes throughout the body. Currently, in the development of atherosclerosis, scientists attach great importance to cholesterol metabolism, so cholesterol is one of the main characteristics of biochemical analysis in the blood [14].

Today, the main way to regulate this level is diet. Pectin supplementation has a positive effect when consumed at 6 g / day, with increasing the dose by 2-3 times the cholesterol level is reduced by 12%. When using special pectins, the content of serum cholesterol is reduced by 19%. In combination with drugs, pectin lowers cholesterol by 31% [15].

Pectin as a dietary fiber. Today, the population consumes a large number of purified, ie free of dietary fiber products. In general, the manufacturer can not change the accepted technological modes of processing of raw materials, technologies of food production, but can add dietary fiber to the recipe, enriching a particular product.

In the last 15 years, no component of food has been the subject of as much research as dietary fiber. Dietary fiber is a plant polysaccharide and lignin that is resistant to hydrolysis by enzymes in the human digestive system. It is proved that the increase in the content of fiber (fiber, pectin, lignin) in the diet reduces the incidence of cancer of the digestive system, in particular, the colon and rectum [13, 16].

Pectin has hemostatic activity in the body. A study of the hemostatic properties of beet pectin and pectates showed that 0.5% and 1% solutions of sugar beet pectin, potassium pectate and sodium when applied topically reduce bleeding time compared to controls by 54% [73 - 75].

Pectin is used as a substitute for blood plasma [76]. 0.5% and 1% pectin solutions are effective plasma substitutes for blood loss in

animals, used to prevent and treat shock. Beet pectin meets all the requirements for plasma substitutes, it does not accumulate in the body, does not cause agglomeration and sedimentation of erythrocytes, does not cause complications [77-79]. When introduced into the blood, most of the pectin is excreted from the body after 36 hours [80, 81].

Pectin, pectinates and pectates are used in microbiology, affinity chromatography of enzyme preparations [82, 83], analytical chemistry [84]. Unlimited possibilities of using pectin and its modifications in the pharmaceutical industry as emulsifiers, drug extenders, antibiotics [85, 86].

Important pharmacological properties of pectin include: the ability to increase the body's immunity, normalize the functions of the gastrointestinal tract, fat metabolism, antimutagenic ability, bactericidal effect on pathogenic microflora, etc. [17, 18].

Based on the above, pectin is one of the most important components of functional and therapeutic nutrition products.

The nature of pectin determines its use as a structuring, thickening, stabilizing factor in the food, pharmacological, perfume and cosmetics industries. Pectin is attracting more and more attention in terms of its properties such as complexing, detoxifying and antioxidant activity. Enriching traditional foods with pectin is one way to turn regular foods into healthy foods [19].

The industry mainly uses dry purified pectin of foreign production for pastille-marmalade, jelly confectionery and canned goods. It is possible to expand the range of pectin products by creating fruit and vegetable products with high pectin content and the introduction of pectin substances in various foods in order to provide products with dietary, preventive and other functional properties [20, 22].

3.2 Food products with pectin

The results of research on the extraction of pectin from plant raw materials, the study of their physical and chemical properties are the basis for the development of technology of fruit and vegetable drinks, purees, pastes, desserts, powders with high pectin content. The peculiarity of the technology is that the stage of purposeful hydrolysis of insoluble protopectin of fresh fruit and berry pomace is provided. After preliminary operations of raw material processing - washing, inspection, grinding, juice separation - the pomace is hydrolyzed by acid-thermal method. As a hydrolytic factor, food grade acids are used or raw materials with high and low acidity are blended. This process allows to increase the content of water-soluble pectin by 25 ... 50% (рис.3.1).

The developed technologies of pectin products have advantages, namely:

use of juice production waste, which makes it possible to completely process fruit and vegetable raw materials;

obtained products, which combine the positive properties of dietary fiber and water-soluble pectin with natural sweeteners that contain biologically active substances and exhibit therapeutic and prophylactic properties;

the introduction of hydrolyzed pectin-containing mass provides the required consistency of the product, its viscosity and homogeneity;

high pectin content improves organoleptic characteristics, enhances fruit aroma, creating a harmonious taste;

pectin-containing products are used directly, or can be semi-finished products in the production of bakery, confectionery, dairy and other products.

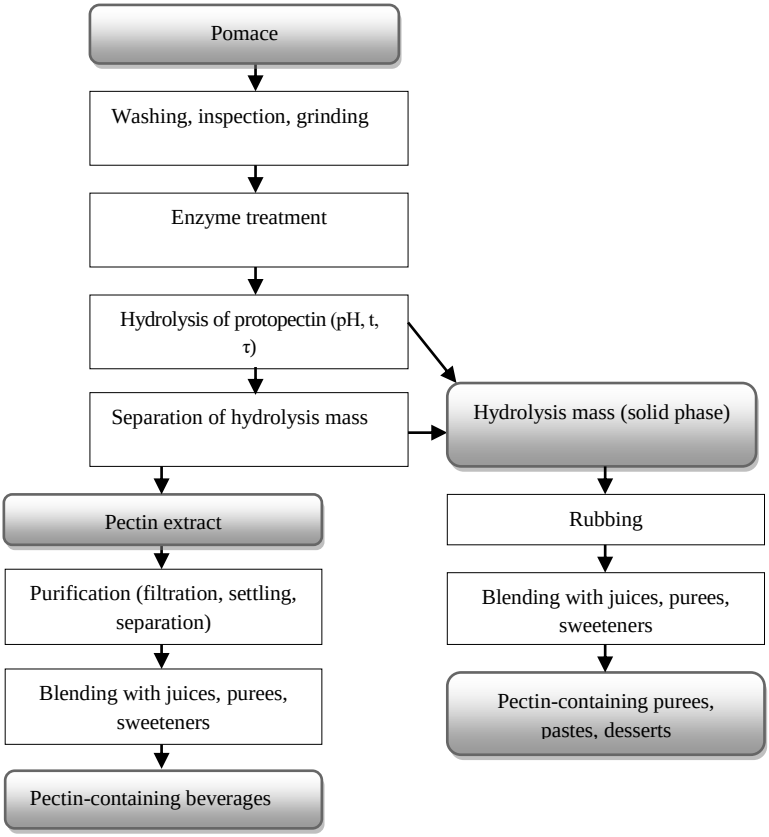

Figure 3.1 - Scheme of pectin-containing products production from fruits and vegetables raw materials

3.2.1 Functional beverages

The modern market is regularly replenished with new health products. The market of functional beverages is developing especially fast, because 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 healthy substances 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 have been identified 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 that are reliably determined using special methods of analysis;

– the introduction of functional ingredients should not reduce the nutritional value of the product [21].

– Vitamins are used for the production of functional drinks. 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 [23]. The specific effect of soluble dietary fiber on the human body is associated with several effects: 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, anticancer 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 beverage, 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, excrete some toxins and heavy metals. Like acidic polysaccharides, they have a synergistic effect with protein molecules, which stabilizes the latter in acidic beverages [24, 25].

Pectin-containing nectars. Specialists of the National University of Food Technologies have developed beverages 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- and trace elements.

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, carrots, apples, currants, apricots, etc..

Pumpkin puree contains polysaccharides (fiber, pectin), monosaccharides and disaccharides (glucose, fructose, sucrose), organic acids (mainly malic). Vitamin composition is represented by vitamins C, B1, B2, carotene. Especially valuable for the child's body vitamin D, which enhances 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 its high content of pectin helps to eliminate cholesterol.

Pumpkin beverages are recommended to include in the diet of patients with hepatitis and cholecystitis, people with gallstones, chronic colitis and enterocolitis, with diseases of the cardiovascular system (hypertension, atherosclerosis with circulatory failure), with 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 absorbed 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 loss of vision. 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, as it has the ability to improve lipid metabolism in the body. Among the minerals are potassium, phosphorus, chlorine and magnesium. In terms of magnesium, carrot raw materials surpass all other vegetable raw materials. It affects vasodilation, activates intestinal motility. Carrot puree has numerous trace elements - aluminum, boron, vanadium, iron, iodine, cobalt, copper, manganese, zinc. Therefore, carrot beverages are recommended for patients with hypothyroidism. 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:

- 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 body cell membranes.

Nectars are made from environmentally friendly raw materials, do not contain synthetic dyes and preservatives.

Table 3.1 - **Organoleptic characteristics of pectin-containing nectars**

Indicator	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 nectars are made. Foreign taste and smell are not allowed
Color	Inherent in the raw material

Table 3.2 - **Physico-chemical parameters of pectin-containing nectars**

Indicator	Value
Mass fraction of dissolved dry matter,%, not less	9,5
Mass fraction of pectin substances,%, 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 more	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 purees, which allows you to get bevarages with pulp and without pulp. Honey, fructose, glucose-fructose or high-fructose syrups can be used as sweeteners in beverages. This allows to people with metabolic disorders, for example, patients with diabetes mellitus to drink beverages [26].

Organoleptic and physicochemical parameters of "Sunski rosy" beverages 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 beverage, 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 beverages "Sunski rosy"**

Indicator	**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 beverage is made. Extraneous taste and smell are not allowed
Color	Homogeneous, corresponding to the color of vegetables, fruits, berries or mixtures thereof, from which the beverage is made

Table 3.4 - **Physico-chemical parameters of beverages "Sunski rosy"**

Indicator	Value
Mass fraction of dissolved dry matter,%, not less	11
Mass fraction of pectin substances,%, not less	0,5
Mass fraction of titrated acids (listed on 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

Biologically active additive phytopectin beverage "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, hypericum, linden, lemon balm, mint, chamomile, dog rose [27, 28].

Table 3.5 – **Organoleptic characteristics of the phytopectin beverage "Suziria Leva"**

Indicator	Characteristic
Appearance	Opaque liquid, slight precipitation is allowed. No extraneous inclusions.
Taste	Sweet and sour, soft, harmonious, with a herbal tone. The bouquet has an apple flavor.

Smell	Characteristically pronounced apple scent with a bouquet of aromas of herbs.
Color	From pink-brown to brown.

Table 3.6 – **Physico-chemical parameters of the phytopectin beverage "Suziria Leva"**

Indicator	Value
Mass fraction of sugar, g/100cm^3	14,0±0,5
Strength, %	12,0±0,5
Mass fraction of extractive substances, g/100cm^3	16,0±0,6
Mass fraction of pectin substances, g/100cm^3, no less	0,5
Mass fraction of titrated acids (in terms of citric acid), g/100cm^3	0,5±0,2
The content of bioflavonoids, mcg/ml, no more	10,0

Institute of Ecohygiene and Toxicology. L. Medved conducted clinical trials and concluded on the clinical aspects of the beverage, according to which the product has a pronounced biological effect.

3.2.2. Canned products

In the canning industry, pectin is used in the production of jelly products: jellies, confitures, jams, as well as health and preventive products (purees, kissels, 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 hydrolyzed and grated pomace - waste from juice production: apple, currant, rowan, carrot with a high content of pectin, which are then blended with fruit or vegetable puree. Organoleptic and physicochemical characteristics are presented in table 3.7 and table 3.8.

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. The technology of making fruit dessert on pectin concentrate, which has a pleasant taste and aroma, beautiful color, jelly consistency, has been developed. The production of dessert is carried out as follows. 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 3.7 - **Organoleptic characteristics of pectin-containing desserts "Barvy Ukrainy" and puree "Darunok"**

Indicator	**Product features**	
	Desserts "Barvy Ukrainy"	**Puree "Darunok"**
Appearance and consistency	Homogeneous rubbed mass without seeds, peel particles and coarse core particles	Homogeneous puree-like mass without seeds of peel particles and coarse core particles
Taste and smell	Inherent in vegetables, fruits or berries from which the	Inherent in vegetables, fruits, berries or mixtures thereof,

	dessert is made	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

Table 3.8 - **Physico-chemical parameters of pectin-containing desserts "Barvy Ukrainy" and puree "Darunok"**

Indicator	**Значення**	
	Desserts "Barvy Ukrainy"	**Puree "Darunok"**
Mass fraction of dry matter,%, not less	45	15
Mass fraction of pectin,%, 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; add 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 - **Recipe for fruit and berry dessert**

Raw materials	Dessert 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 for direct consumption and for the manufacture of most confectionery products. Candied fruits are based on carbohydrates, as well as organic acids and minerals.

The technology of pectin-containing candied fruits is based on the process of converting protopectin into soluble form. The raw material is cut into pieces of 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 times infusing them in sugar syrup until the candied sugar is completely saturated with 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,

watermelon peels 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, characteristic of the type of raw material. Color - provided 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 peels of watermelons, melons, pumpkins, carrots, beets, zucchini - 80%. The content of total sugar per invert is 75% and 72%, respectively.

Pectin-containing vegetable products: ketchup "Pectodar", sauces "Darunok Poliv" and "Katran" (TS U 18019595-29-95) [30].

The basis of ketchup "Pectodar" and sauce "Darunok Poliv" are tomato products, for sauce "Katran" is horseradish. Pectin, extracts of beet and carrot, sugar, salt and spices are included in the ketchup "Pectodar" recipe.

Table 3.10 - **Organoleptic characteristics of vegetable pectin products**

Indicator	Characteristics of pectin products		
	Ketchup "Pectodar"	**Sauce "Darunok Poliv"**	**Sauce "Katran"**
Appearance and consistency	Homogeneous rubbed mass without seeds, peel particles and coarse core particles. The presence of small particles of spices, particles of greens is allowed	Homogeneous rubbed mass without seeds, peel 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 tomato products, 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 - **Physico-chemical characteristics of vegetable pectin products**

Indicator	**Ketchup "Pectodar"**	**Sauce "Darunok Poliv"**	**Sauce "Katran"**
Mass fraction of pectin substances,% not less	0,5	0,5	0,5
Mass fraction of dry matter,% not less	15	15	15
Mass fraction of chlorides,%	1,5…2,5	1,5…2,5	1,5…2,5
Titrated acidity (in terms of malic acid), in% 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; in "Katran" sauce is added pectin, table beet extract, sugar, salt, spices..

3.2.3. Confectionery

Due to the optimal application possibilities and numerous advantages, pectins are becoming increasingly important in the confectionery industry as texture-forming 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 production 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 gel formation, 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 natural taste of fruit raw materials or added flavors is well manifested in the products. [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 Technologies [34, 35]. The technology is implemented at the enterprises for processing of fruit and vegetable raw materials and is made according to the developed normative and technical documentation (TS U 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**

Indicator	Value
Mass fraction of dry matter,%	6,4±0,2%
Mass fraction of pectin substances,%	3,0±0,2%
Active acidity, pH	3,0±0,2

Given the fact that pectin is used as a gelling agent in the production of marmalade products, the ability of pectin concentrate to gel fomation and the effect of sugar and acid on the strength of gems was studied. The results of the study are presented in Fig. 3.2.

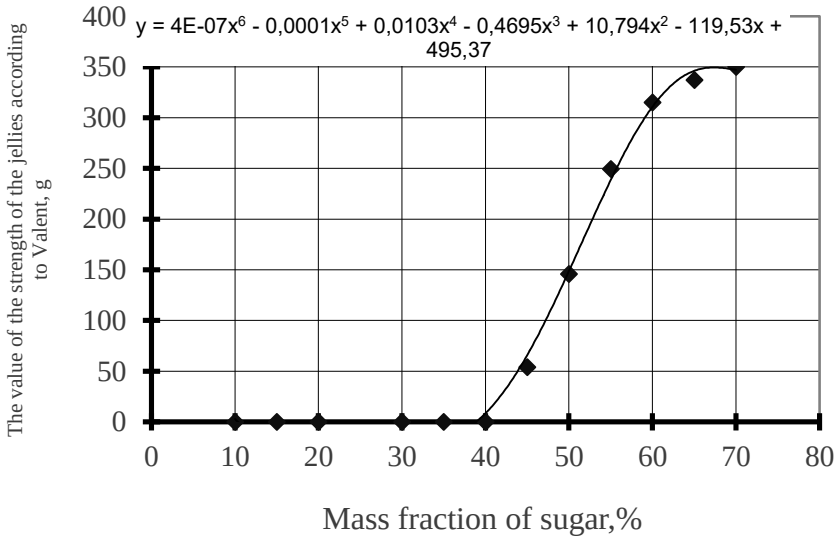

Figure 3.2 - Dependence of jellies strength on the concentration of sugar in pectin-sugar syrup

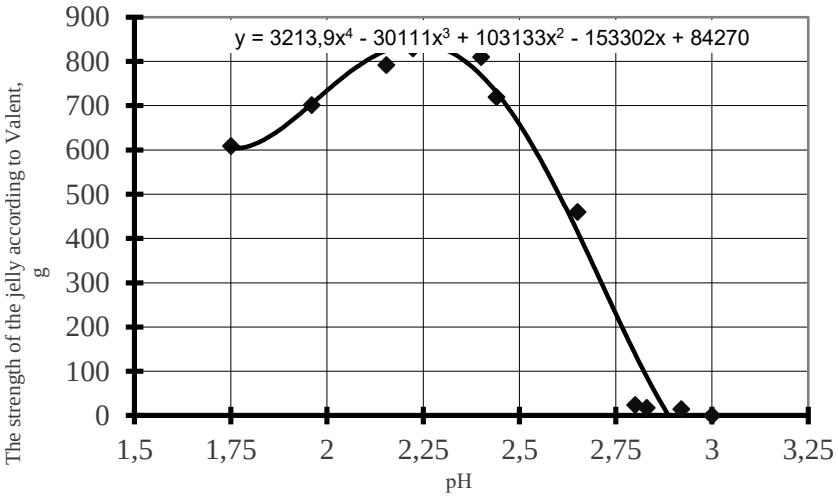

Figure 3.3 - Dependence of the strength of the jellies on the change in pH of the jelly mass

According to traditional technology, the recipe of pectin-based jelly marmalade includes the following recipe components: pectin, sugar, molasses starch, 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).

Marmalade. The development of the technology of jelly marmalade made using apple pectin concentrate is based on the obtained research data [36].

Preparation of raw materials is carried out similarly to the classical technology: sugar is sifted, citric acid solution and pectin concentrate are filtered.

Half of the sugar in the recipe is added to the pectin concentrate.

Table 3.13 - **Recipe of jelly marmalade based on APC**

Name of raw materials	Mass fraction of dry matter, %	Expenses of raw materials for the production of 1000 kg of products	
		actually, kg	in dry matter, kg
Pectin concentrate	6,40	900,0	58,0
Sugar	99,85	520,0	519,0
Starch molasses	78,00	170,0	133,0
Food essence	0,00	00,6	0,00
Food dye	0,00	00,1	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

The mass is boiled to a dry matter content of 55 ... 60 %. Then the second half of sugar is entered and boiling to dry matter content of 68...70 % proceeds. The temperature of the mass after boiling is approximately 107...108 ºC, then it is cooled to a temperature of 70...75 ºC, 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...35 ºC for 1...2 h at a humidity of 20...30 %. A

crust is formed on the surface of the marmalade, which increases the adhesive forces, which promotes better adhesion of sugar when sprinkled. After that, the marmalade is sprinkled with granulated sugar and sent for drying, which takes place at a temperature of 40...45 ºC for 20...22 h at a humidity of 20...30 %. The finished marmalade is packed in boxes and sent for sale.

The technological scheme of making jelly mold marmalade using apple pectin concentrate is presented in Figure 3.4.

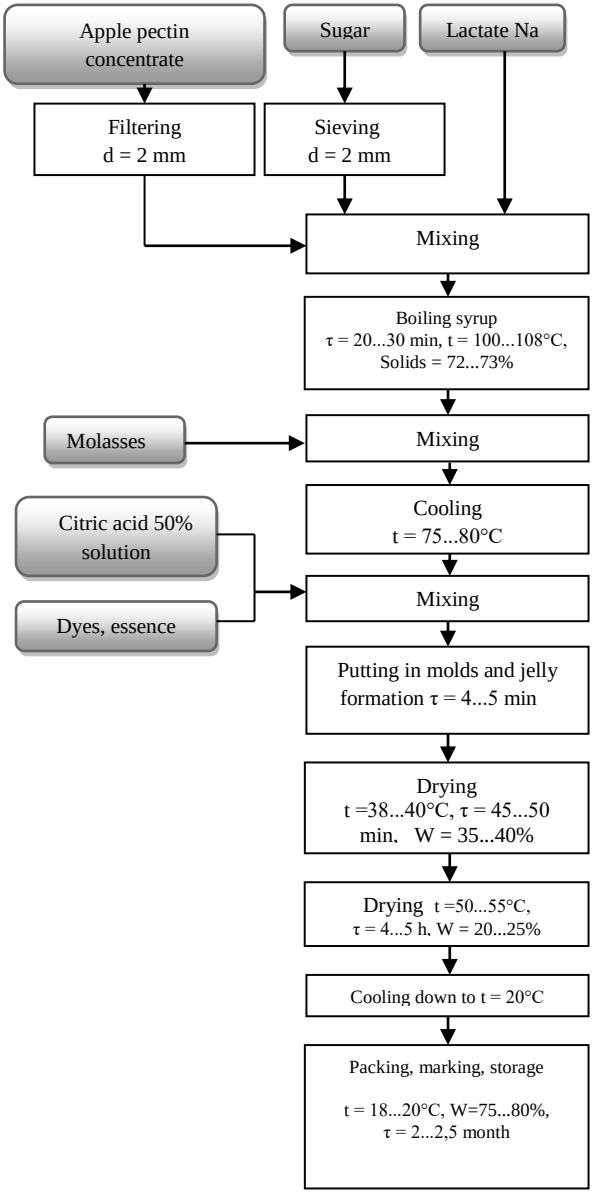

Figure 3.4 - Technological scheme of jelly marmalade production using APC

Based on the analysis of the production 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 saving of time is 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 economically advantageous not only by reducing the cost of raw materials, but also by reducing the duration of the technological process of jelly marmalade production.

Research of structural and mechanical properties. Based on the obtained samples, the analysis and comparison of structural and mechanical properties of the obtained marmalade based on APC and traditional marmalade based on dry apple pectin was performed. The research was conducted on the scales of Kargin-Sokolova, the results are presented in Fig. 3.5.

Based on the obtained dependences, the main necessary rheological characteristics were calculated and their analysis and comparison were performed.

Determination of c. The springiness of the obtained samples is calculated by the formula:

$$\text{Пр} = \frac{\varepsilon_o}{\varepsilon_m} \cdot 100 \quad (3.1)$$

where ε_o – springy conditional-instantaneous deformation, which instantly occurs 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.

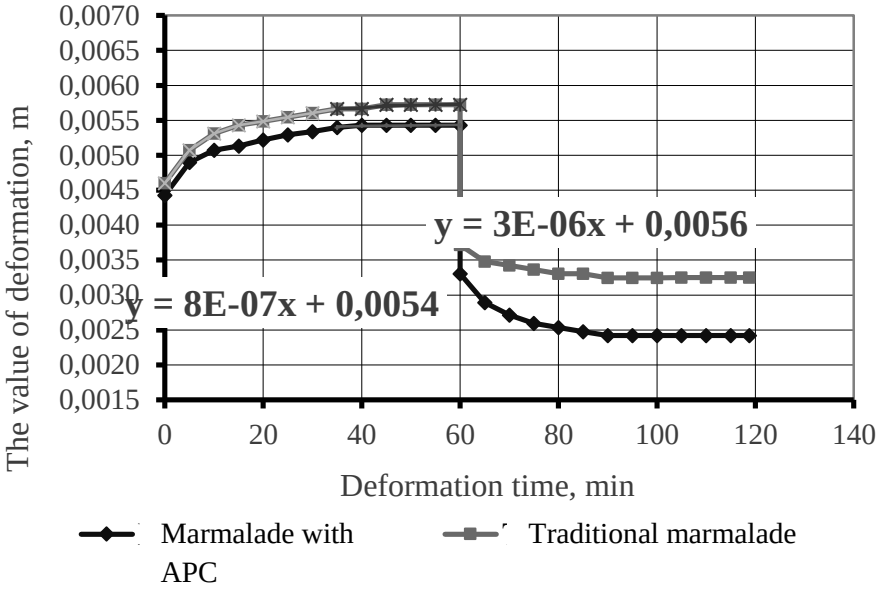

Figure 3.5 - Rheological characteristics of marmalade jellies

$$\varepsilon_m^{APC} = 0{,}0054(m)\ \ \varepsilon_m^{trad.} = 0{,}0057(m)$$

$$\varepsilon_0^{APC} = 0{,}0044(m)\ \ \varepsilon_0^{trad.} = 0{,}0046(m)$$

$$Пр^{APC} = \frac{\varepsilon_0^{APC}}{\varepsilon_m^{APC}} \cdot 100 = \frac{0{,}0044}{0{,}0054} \cdot 100 = 81{,}48 \pm 0{,}4,$$

$$Пр^{trad.} = \frac{\varepsilon_0^{trad.}}{\varepsilon_m^{trad.}} \cdot 100 = \frac{0{,}0046}{0{,}0057} \cdot 100 = 80{,}70 \pm 0{,}4$$

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, determine the stress on the sample, which was calculated by formula 3.3.

$$P = \frac{F}{S} = \frac{F}{\pi r^2} = \frac{0,075}{3,14 \cdot 0,004^2} = 1492,8(Pa) \tag{3.3}$$

then

$$E_s^{APC} = \frac{P}{\varepsilon_0^{APC}} = \frac{1492,8}{0,0044} = 339,3(kPa/m),$$

$$E_n^{trad/} = \frac{P}{\varepsilon_0^{trad/}} = \frac{1492,8}{0,0046} = 324,5(kPa/m).$$

Determination of elasticity. Elasticity is calculated by the formula:

$$E = \frac{\varepsilon_{he}}{\varepsilon_{se}} \cdot 100 \tag{3.4}$$

where ε_{se} – specific elastic deformation - completely reversible relative deformation: $\varepsilon_{se} = \varepsilon_0 + \varepsilon_{he}$;

ε_{he} – highly elastic deformation - relative deformation that gradually disappears after stress relief: $\varepsilon_{he} = \varepsilon_{se} - \varepsilon_0$;

$$\varepsilon_0^{APC} = 0{,}0044(m) \qquad \varepsilon_0^{trad} = 0{,}0046(m)$$

E_{se} 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.

$$\varepsilon_{se}^{APC} = 0{,}0051(m) \qquad \varepsilon_{se}^{trad} = 0{,}0055(m)$$

So

$$\varepsilon_{he}^{APC} = 0{,}0051 - 0{,}0044 = 0{,}0007(m)$$
$$\varepsilon_{se}^{trad} = 0{,}0055 - 0{,}0046 = 0{,}0009(m)$$

The elasticity of marmalade samples was calculated on the basis of data on specific elastic deformation and highly elastic deformation.

$$E^{APC} = \frac{\varepsilon_{he}^{APC}}{\varepsilon_{se}^{APC}} \cdot 100 = \frac{0{,}0007}{0{,}0051} \cdot 100 = 13{,}72 \pm 0{,}4,$$

$$E^{trad} = \frac{\varepsilon_{he}^{trad}}{\varepsilon_{se}^{trad}} \cdot 100 = \frac{0{,}0009}{0{,}0055} \cdot 100 = 16{,}36 \pm 0{,}4$$

The modulus of elasticity is calculated by the formula:

$$E_e = \frac{P}{\varepsilon_{he}}, \qquad (3.5)$$

$$E_e^{APC} = \frac{P}{\varepsilon_{he}^{APC}} = \frac{1492,8}{0,0007} = 2,13(MPa/m),$$

$$E_e^{trad} = \frac{P}{\varepsilon_{he}^{trad}} = \frac{1492,8}{0,0009} = 1,66(MPa/m).$$

Thus, the relative elasticity and modulus of elasticity of marmalade made on the basis of APC and marmalade made by traditional technology are almost indistinguishable.

Determination of plasticity. 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_{pl} – residual (plastic) deformation that does not disappear after removal of the applied stress for an infinitely long time: $\varepsilon_{res} = \varepsilon_{pl}$.

$$\varepsilon_{pl}^{APC} = 0,0024(m) \qquad \varepsilon_{pl}^{trad} = 0,0033(m),$$

$$\varepsilon_m^{APC} = 0,0054(m) \quad \varepsilon_m^{trad} = 0,0057(m),$$

$$Pl^{APC} = \frac{\varepsilon_{pl}^{APC}}{\varepsilon_{m}^{APC}} \cdot 100 = \frac{0,0024}{0,0054} \cdot 100 = 44,44 \pm 0,4,$$

$$Pl^{trad} = \frac{\varepsilon_{pl}^{trad}}{\varepsilon_{m}^{trad}} \cdot 100 = \frac{0,0033}{0,0057} \cdot 100 = 57,9 \pm 0,4.$$

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 marmalade under study 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 are developed. Organoleptic evaluation of the obtained samples and existing ones on the market was carried out. It is determined that the organoleptic indicators of the obtained samples are not inferior to the samples of marmalade made of pectin and present on the market of Ukraine.

Marmalade technology "Orange and lemon particles" based on apple pectin extract 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 dry matter content of 73…74 %, cooling to 60…65 °C, adding citric acid, sodium lactate, essences and dyes, mixing and casting molds, keeping 1,0…1,5 h for jelly formation, removal, drying to the dry matter content of 79%, glazing with chocolate glaze, cooling and packing [38].

Jelly antimutagenic product. Jelly antimutagenic product contains natural juice of fruits of medicinal plants, apple pectin concentrate, sugar, sodium lactate in the following ratio of ingredients:

natural juice of fruits of medicinal plants	40 – 60 %,
apple pectin concentrate	25 – 40 %,
sugar	40 – 55 %,
sodium lactate	0,3 – 0,5 %.

The product is made of natural juice with the pulp of fruits 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.

Natural juice with the pulp of the fruits of medicinal plants is mixed with apple pectin concentrate and sugar, boiled for 3… 5 minutes, added sodium lactate and submitted to the formation.

The use of natural juices with the flesh of medicinal plants 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].

Pastille products. Pastille products are obtained by whipping boiled fruit and berry puree with sugar and egg white and mixing with gelling agents. They have a foam-like structure reinforced with gelling agents. Foams are a dispersed system consisting of cells filled mainly with air and separated from each other by thin films of dispersion medium. In pastille 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. Egg white is used as a surfactant to facilitate the whipping process and to obtain more stable foams. The low surface tension of egg white reduces 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 dry matter content and limited viscosity are unstable systems. Under the action of surface tension and fluid flow, the carcass films become thinner and gradually break down. To give the system more stability immediately after beating the mass is mixed with hot sugar syrups containing structurants (agar, agaroid or pectin). As the shell cools, the foam frame becomes semi-rigid. Special types of structuring agents 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 which is observed in whipped products based on agar. Depending on the method of molding, pastille products are divided into carved (pastila) and molded (marshmallows) [45,46].

Marshmallow. 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].

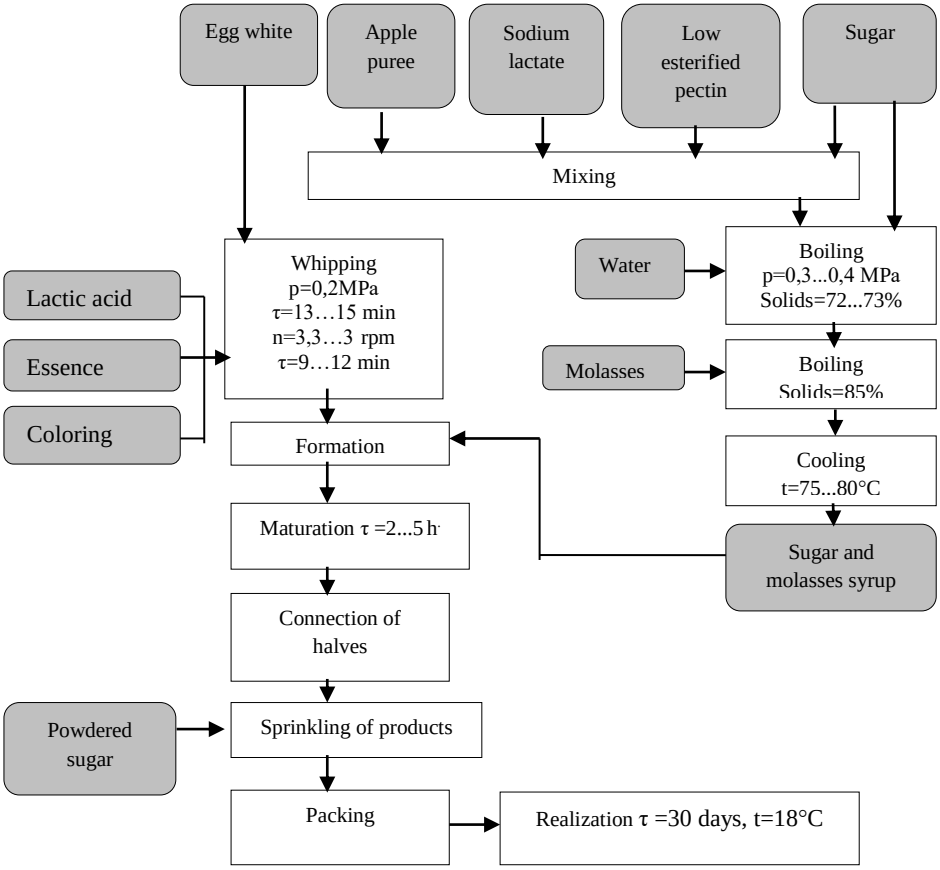

Figure 3.6 - Technological scheme of marshmallow production

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 sugar, 61.39 kg of egg white, 7.88 kg of lactic acid, 0.47 kg of vanilla essence and beat the resulting mixture for 13…15 minutes under a pressure of 0.2 MPa, add at the end of beating sugar-molasses syrup weighing 554.53 kg, which boiled with 330.14 kg of sugar and 187.17 kg of molasses to a dry matter content of 83…85% and a temperature of 75…80 °C, form products in the form of hemispheres, stand for 2…5 h at a temperature of 20…25 °C, connect the halves, sprinkle with powdered sugar weighing 29.75 kg and pack.

Pastila. Obtaining a pastila based on low-esterified pectin in the form of a fine powder, which is not used in the confectionery industry, provides an expansion of the range of sugar confectionery products with a foamy gelatinous structure of the pastila type, the use of new types of functional raw materials, reduction of energy consumption and increase of efficiency of technological process due to reduction of number of technological stages [49].

Apple puree weighing 639.24 kg is mixed with 492.64 kg of sugar, 24.45 kg of egg white and beat the resulting mixture for 10… 12 minutes, at the end of beating add sugar-pectin-molasses syrup weighing 348.61 kg, cooked from 225.42 kg of sugar, 7.09 kg of low-esterified pectin, 59.32 kg of molasses and having a temperature of 85… 95 ° C, add 6.27 kg of lactic acid, 0.63 kg of vanilla essence, mix, form layer, stand for structure formation, cut into cubes, sprinkle with powdered sugar weighing 45.87 kg, dried in the first stage for 2.5… 3 h at an air temperature of 40… 45 ° C and humidity of 40… 45%, for the second - 2 h at a temperature of 50… 55 ° C and humidity of 20… 25%, cooled and packed.

The technology of pastila with the use of apple pectin concentrate has been developed [48].

Production of Turkish delight (lokum) and fruit-whipping candies. The range of confectionery products with a foam structure is quite diverse, however, sweets and oriental sweets occupy 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-beating part of the recipe mixture, thus forming a thick foam with microscopically small air bubbles surrounded by a thin film of viscous fruit-protein-sugar mixture. Under the action of surface tension, the individual bubbles in the foam mass connect, increasing in size, resulting in a degree of dispersion decreases, increasing in size, resulting in a decrease in the degree of dispersion, the foam decreases. To prevent this process, surfactants, usually egg white, are added to the film that wraps the air bubbles.

Studies suggest that it is possible to replace egg white up to 30% of the prescription amount with 10% solution of low-esterified pectin (LEP) while maintaining yield and increasing the stability of foam systems.

Sugar-starch-molasses syrup, the specific weight of which in the recipe 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 fruit whipped mass (semifinished product for candies), which ensures high quality products, is expressed according to 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 gelling component on the viscosity of starch solutions was studied (Fig. 3.6).

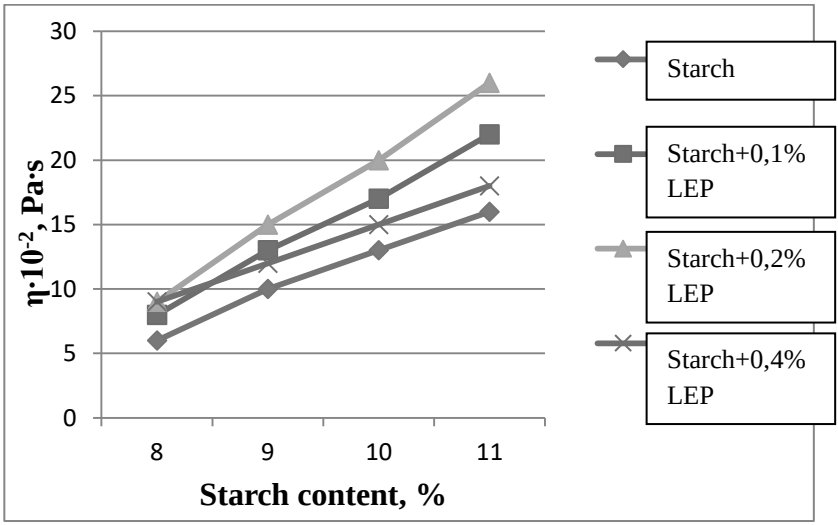

Figure 3.6 - Dependence of the viscosity of the modified starch solution on the concentrations of low-esterified pectin (LEP)

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 whips semi-finished products - (8.3 ... 8.5): (53 ... 55): 0.2%.

Table 3.15 - **The effect of low-esterified pectin on the strength of sugar-starch gels**

Concentration of LEP, %	**Percentage of starch and sugar**		**Sugar concentration, %**	**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	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				327 288	332 301	345 312

Data analysis allowed to choose the ratio of prescription components, in which the products have high organoleptic characteristics, and their physico-chemical parameters are as close as possible to products made by traditional technology. For lokum, the prescribed amount of starch, sugar and LEP is defined as 9.3: 68: 0.2, for candy - 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 dry matter, %	The amount of raw materials per 1 ton of finished product, kg			
		lokum		fruit whipped candies	
		actually	in dry matter	actually	in dry matter
Sugar granulated	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 white	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
Yield		1000,0	778,0	1000,00	750,00

Lokum. The technology is based on the use of LEP as a structurant [55].

The proposed method of obtaining Turkish delight includes mixing LEP with granulated sugar, apple puree, boiling the system to 74…76 % of dry matter, beating 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 layers into 20×25×40 mm, sprinkled with powdered sugar with vanilla and packaging.

The chemical composition of the proposed products is slightly different from the traditional one. The change in the mass fraction of dry matter 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 production of lokum (Fig. 3.7) using LEP includes stages of preparation of raw materials, preparation of LEP solution and starch-sugar-molasses syrup, beating of mass, maturation and formation of products, packing.

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 appliance. The starch is combined with granulated 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 add molasses.

Starch-sugar-molasses syrup cooled to 75...80 °C, egg white mixed with LEP solution (ratio of LEP and water is 1: 9) is fed into the whipping machine and beaten for 7...8 minutes. At the end of beating, add blackcurrant broth, citric acid and essence and continue beating for 2 ...3 min.

The finished mass is fed to the molding, poured into trays and left in the shop for 18...20 hours. After maturation, the whipped mass is sprinkled with powdered sugar and cut into bars measuring 40 × 40 mm. After cutting, sprinkle with powdered sugar, packed and stored.

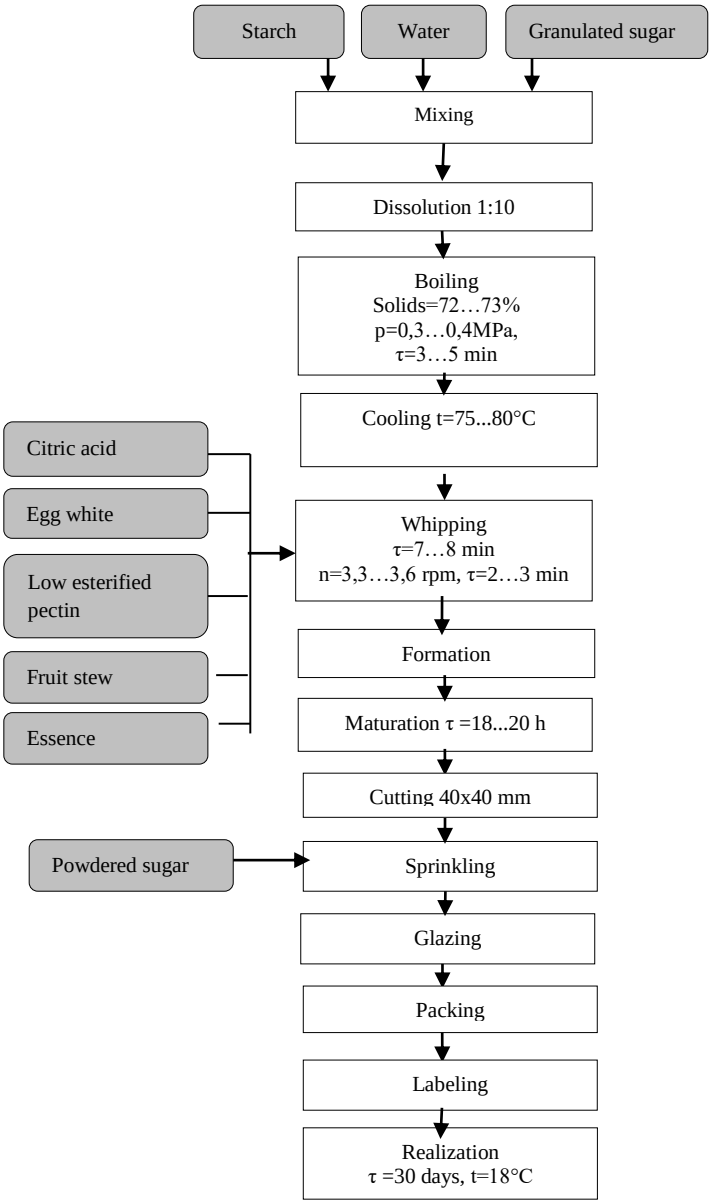

Figure 3.7 - Technological scheme of lokum production

The technology of production of fruit-whipped candies (Fig. 3.8) includes stages of preparation of raw materials, preparation

of LEP solution and starch-sugar-molasses syrup, preparation of whipped mass, body formation, candy glazing, cooling, packaging and labeling [50].

Preparation of a solution of LEP, 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 shop for 18 ... 24 hours. After maturation, 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 h 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). Physico-chemical indicators of products are determined. Their values correspond to the norms, namely: for Turkish delight - humidity 19...20%, mass fraction of reducing sugars - up to 40%, total acidity - not less than 0.2%; for candies based on fruit-whipped semi-finished products - humidity 22...25%, mass fraction of reducing sugars - up to 25%, total acidity - not less than 0.35%.

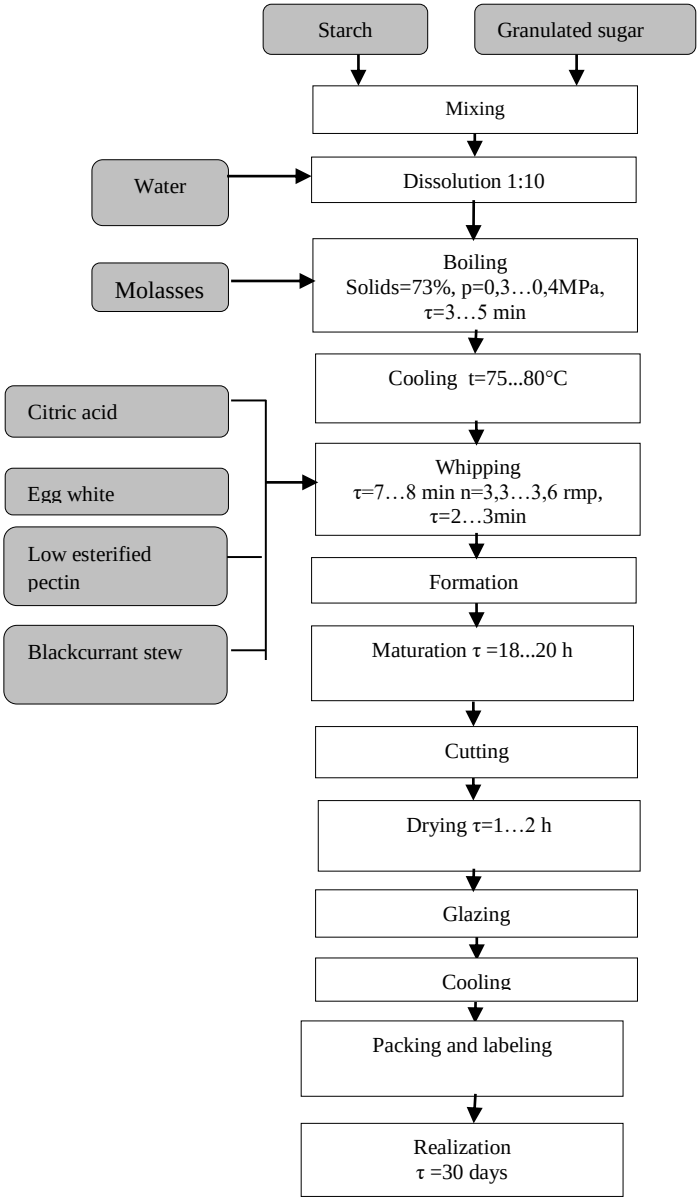

Figure 3.8 - Technological scheme of fruit-whipped candies production

The proposed recipes and technologies of Turkish delight and candies with the use of LEP make it possible to reduce the egg white content by up to 20% of the total weight of the product without compromising organoleptic and physicochemical performance, increase the stability of whipping systems, and thus ensure high quality products.

Candies. Recipes of candies (RC) made by coextrusion “Zolota sopilka” (RC 18 Ukraine 222-K-98), “Charivni barvy” (RC 18 Ukraine 221-K-98) with the use of pectin-containing purees, desserts and powders have been developed. Candy "Shchedryk smak" (RC 18 Ukraine 219-K-98) and "Shchedryk smorodynka" (RC 18 Ukraine 220-K-98) are produced with the addition of pectin-containing raw materials and extrusion products, candied fruits, nuts [52,53].

The basis of "Tsytrusovi" candy technology is the use of low-esterified pectin, which helps to expand the range of sugary confectionery products with a jelly-like structure of candy type. Preparation of "Tsytrusovi" candies includes stages of mixing dissolved in water low-esterified pectin, sugar, molasses, citrus stew, apple puree and lactic acid, boiling the mass to a dry matter content of 75%, casting in the molds, maturation 1.0…1.5 h for jelly formation, extraction, chocolate glazing, cooling and packaging [51].

Jelly-like semi-finished products for flour confectionery. On the basis of researches of functional-technological properties of pectin-containing purees, juices the assortment of thermostable stuffings, jelly glaze is developed and the technology of their production is scientifically proved: 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	Dry matter, %	Expenses of raw materia, kg			
		for loading		per 1 ton of finished product	
		actually	in dry matter	actually	in dry matter
Carrot hydrolyzed puree	11,0	54,7	6,02	746,35	82,1
Granulated 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
Yield	68,0	73,09	49,87	1000,00	680,00

Table 3.18 - **Recipe of the filling "Karotynka-yabluko"**

Name of raw materials	Dry matter, %	Expenses of raw materia, kg			
		for loading		per 1 ton of finished product	
		actually	in dry matter	actually	in dry matter
Carrot hydrolyzed puree	11,0	33,0	3,63	430,87	47,4
Hydrolyzed apple puree	10,0	19,0	1,9	248,08	24,81
Granulated 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
Yield	68,0	76,59	52,08	1000,00	680,00

Table 3.19 - **Recipe of the filling "Harbuzynka"**

Name of raw materials	**Dry matter, %**	**Expenses of raw materia, kg**			
		for loading		**per 1 ton of finished product**	
		actual ly	**in dry matter**	**actual ly**	**in dry matter**
Pumpkin hydrolyzed puree	11,0	57,0	6,27	824,67	90,71
Granulated sugar	99,85	41,5	41,44	600,45	599,55
Low-esterified citrus 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	1,3
Total	-	100,00	49,07	1446,86	709,94
Yield	70,0	69,1	48,38	1000,00	700,00

Table 3.20 - **Recipe for jelly glaze "Karotel"**

Name of raw materials	**Dry matter, %**	**Expenses of raw materia, kg**			
		for loading		**per 1 ton of finished product**	
		actual ly	**in dry matter**	**actual ly**	**in dry matter**
Carrot hydrolyzed juice	8,5	35,0	2,98	395,09	33,58

Highly 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
Granulated 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
Yield	70,00	88,73	62,11	1000,00	700,00

New types of semi-finished products with a jelly-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" and glaze jelly "Karotel".

Technological scheme of production of fillings on the basis of carrot, carrot-apple, pumpkin hydrolyzed puree provides preparation of raw materials for production, preparation of fillings, their cooling and packing (fig. 3.9).

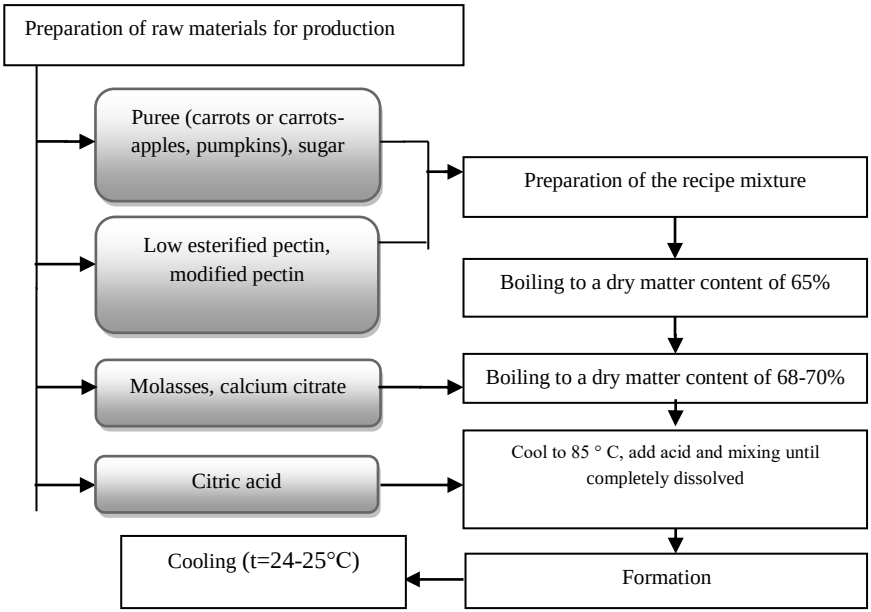

Figure 3.9 - Technological scheme of preparation of fillings based on carrot, carrot-apple, pumpkin hydrolyzed puree

Preparation of raw materials. The sugar is sifted through a sieve with holes no larger than 3 mm in diameter and passed through magnets to remove metal impurities.

Carrot, apple, pumpkin hydrolyzed puree made in accordance with TS U 15.3 - 35422486 - 002: 2009 "Fruit, vegetable, fruit-vegetable puree" was used in the preparation of fillings. 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 the dry mixture for each weight part of pectin take 3…5

parts by weight of granulated sugar, all this is thoroughly mixed. Spent on the preparation of dry mixture of granulated sugar is subtracted from the total prescribed amount of granulated 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 fillings. Pectin-containing puree is mixed with sugar, pectin or a mixture of pectin and modified starch, which is dosed according to the recipe in the appropriate amount to the weight of the puree.

When preparing fillings based on CHP, the ratio between CHPand sugar is 58:42, the amount of LM pectin ARA 300FB is 1.0% by weight of the filling.

When preparing the filling based on CAHP, the ratio between CHP, AHPand 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 fillings based on 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 fed by boiling to a dry matter content of 65%, then add 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 boil the mass to dry matter content 68…70%. When the mass has cooled to 80…85 °C, add citric acid and mix 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).

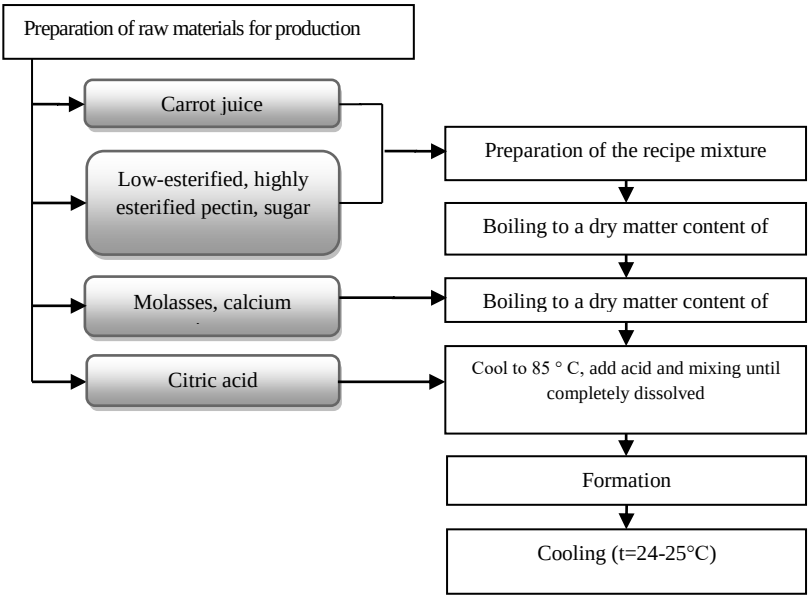

Figure - 3.10 Structural technological scheme of preparation of jelly glaze based on carrot pectin juice

Preparation of raw materials. The sugar is sifted through a sieve with holes no larger than 3 mm in diameter and passed through magnets to remove metal impurities.

The development of jelly glaze technology used carrot hydrolyzed juice without pulp, which is produced in accordance with TS U 15.3-35422486-001: 2009 "Juices, nectars, juice-containing fruits beverages, vegetables, fruit-vegetable, vegetable-fruit" [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 diameter of not more than 2 mm.

The gelling ability of pectin is pre-tested by the laboratory. To prepare the dry mixture for each weight part of pectin take 3…5 parts by weight of granulated 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 granulated sugar, is added to the carrot juice and mixed thoroughly until completely dissolved. The prepared mixture is boiled to a dry matter content of 55%, then added molasses, calcium citrate and boiled the mass to a dry matter content of 70%. When the mass has cooled to a temperature of 80…85 ° C, added citric acid and mixed thoroughly again. The finished mixture is formed and cooled to 20… 25 ° C.

The finished semi-finished product is a strong 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 products transparency. Such masses retain their shape well and can be used to decorate flour confectionery.

3.2.4 *Culinary products*

The range of sweet jelly dishes is quite wide, but special attention is paid to dishes with a foamy structure, in particular, sambuc [57].

Sambuc. Sambuc is a dish with high organoleptic characteristics and biological value. In addition, sambuc does not contain exclusively seasonal raw materials and is therefore a universal dish for cooking in restaurants all year round.

High quality of this product is largely determined by the stability of the foam system, which is obtained by beating the recipe mixture. Sambuc is a homogeneous, loose, finely porous mass with an springy consistency. The foamy structure of the dish is provided

by pectin substances of fruit raw materials and egg whites, springy consistency - gelatin. The sucrose content is 18…20% [59].

In fig. 3.11 shows the technological scheme of preparation of sambuc using low-esterified pectin.

In order to expand the range of dietary low-calorie sweet cold dishes with a foamy gelatinous structure developed sambuc technology using LEP and sugar substitutes - saccharin.

It is known that low-esterified pectins form a gelatinous structure in the presence of calcium ions in a wide range of pH of the process medium with or without added sugar.

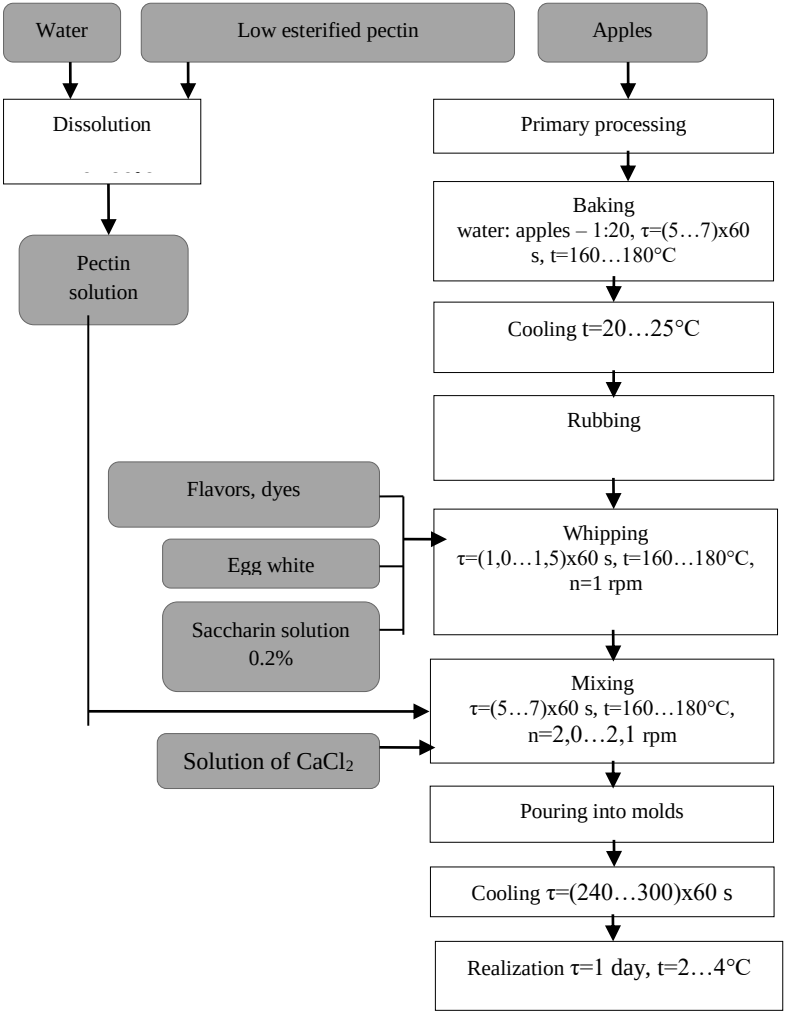

Figure 3.11– Technological scheme of sambuc preparation using low-esterified pectin

According to the developed technology, apple puree obtained from baked apples is cooled, beaten with egg white, 0.2% saccharin solution, flavors and dyes 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 of restaurants, expands the range of dietary low-calorie sweet cold dishes with foamy gelatinous structure like cream, use new types of 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, grinding the mixture, adding saccharin solution, adding calcium chloride in saturated solution, heating to 70…80 °C, filtering, adding vanillin, cooling to 40…50 °C and adding the resulting 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 low-calorie sweet cold dishes with foamy jelly-like structure mousse type, reduce energy consumption and increase the efficiency of the process by reducing the number of technological stages (mixing pectin with sugar, dissolution). The proposed method of obtaining mousse includes boiling lemon zest in water for 3…5 minutes, filtering, adding saccharin in 0.2% solution, powdered LEP, adding squeezed lemon juice, dyes, flavors and saturated calcium chloride solution, cooling to 30…40 °C, beating until the mixture turns into a loose mass,

pouring into molds, keeping for 3…5 hours at a temperature of 10…14 °C for structuring the system, removing from the molds, watering with cherry syrup [58].

Jelly. Jelly is obtained by mixing apple pectin concentrate with fruit juice or fruit decoction and granulated sugar, boiling the mixture for 3…5 minutes, then add dyes, flavors, citric acid, poured into molds and kept 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].

3.2.5 *Dairy 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 well-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 and jelly fillers, sauces and liquid concentrates, can be used in the production of fruit yogurts, fruit-dairy desserts with fruit fillers.

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 can be seen 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 by pectin has been used previously, for example, in cheese production. 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), as a result, 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 3.6) 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].

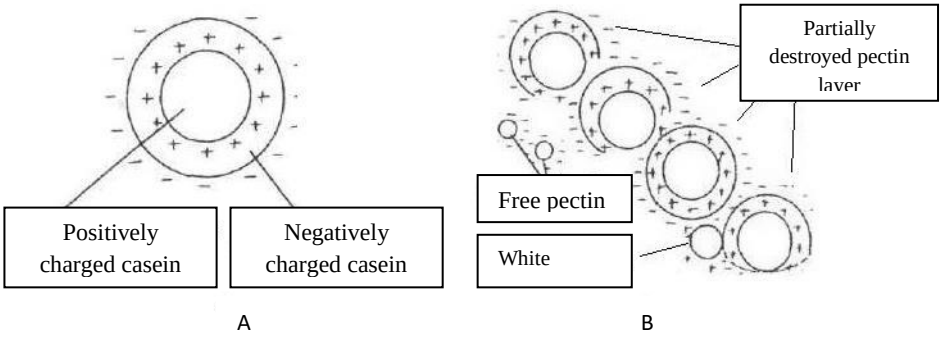

Figure 3.12 - Stabilizing effect of pectin on dairy products

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 excessive 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 precise degree of esterification - within 70%, as pectins with a lower degree of esterification are able to react with calcium in milk, and pectin molecules with more with a high degree of esterification have fewer negatively charged carboxyl groups and are therefore less reactive. The dosage of pectin depends on the content of milk proteins. Optimal dosage does not affect the viscosity of the product, pectin overdose impairs taste.

An important factor that ensures the stability of the product is the pH value 4. Lowering the pH by 0.5 units leads to a sharp decrease in stability. Thus, the pH values of fermented milk products and their acidity significantly affect the dissociation of pectin and, consequently, 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 can vary from viscous-fluid to strong, depending on the dosage of pectin. 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

pectin preparation 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 can be increased 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 soluble form. Thus, the concentration of calcium ions reacting with pectin increases sharply. The formed calcium pectate precipitates.

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 the use in the recipe of yogurt with 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 can not stabilize the product. This is due to a sharp decrease in the degree of dissociation of carboxyl groups of pectin at pH below 3.5, which, in turn, reduces 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 pH above 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 fruit juice (if used). Fruit juice with a low total acidity adversely affects the stability (there is a risk of whey separation) of the finished product. To correct this negative effect, it is needed to increase the dose of pectin.

Milk protein content. It has been empirically established that for satisfactory stabilization of yogurt from milk with a protein content of 4%, it is sufficient to use 0.5% pectin in terms of weight of finished yogurt. At higher concentrations of milk proteins it is necessary to increase the dosage of pectin by the 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 dosing 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).

Increasing the dosage of pectin can be carried out to a level of 0.7% in terms of weight of the finished product.

Products "Pektolin", "Pektolakt" and beverage "Pektynovyi". 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 "Pektolin", "Pektolakt" and beverage "Pektynovyi"**

Indicator	Characteristic		
	"Pektolin"	"Pektolakt"	"Pektynovyi"
Appearance and consistency	Homogeneous liquid with a broken or intact clot, slight viscosity and slight whey separation are assumed	Homogeneous liquid-drink, with the consistency of kissel, the system - dessert	Homogeneous liquid-drink
Taste and smell	Pure sour-milk with taste and aroma of filler	Sweet and sour, whey with the taste and aroma of the filler	Sweet and sour, 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

"Pektolin" 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 "Pektolakt" is a mixture of whey with skim milk and pectin concentrate, to which sugar and starch are added. The filtered whey and skim milk are pasteurized and cooled. Starch is dissolved in chilled skim milk. The whey is mixed with pectin

concentrate, heated to 65...70 °C, added granulated sugar, heated to 90 °C and added the dissolved starch. The mass is incubated for 5...0 minutes. Thoroughly mixed and cooled product is packaged.

The recipe of the beverage "Pektynovyi" includes whey, pectin, sugar and aromatic additives. Pectin is thoroughly mixed with sugar in a ratio of 1:1, poured the prescribed amount of water at a temperature of 40...45 °C and left for 3...4 hours to swell the pectin, stirring the mixture periodically. Then filtered whey is introduced into the mixture with stirring, 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 skim or normalized milk by fermentation with yeast 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, "Lali" pasta 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 sharply salty taste with a hint 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.

3.2.6 *Pectin-containing powders*

The main source of dietary fiber is plant raw materials, in particular, secondary plant resources: bran grain crops pomace of fruits and berries, etc. Beet pulp - a waste of sugar production - is of interest as a source of dietary fiber. Pulp 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. Pectic 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 therapeutic, prophylactic 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, condition of the cardiovascular system and digestive organs) allows them to attribute as dietary supplements. All these properties are inherent in beet pectin.

Researches on creation of polysaccharide functional complexes from beet pulp for reception of dietary and food additives were carried out. In order to obtain water-soluble pectin, beet pulp was subjected to acid-thermal hydrolysis and dried. This polysaccharide complex has increased moisture retention, complexing and sorption capacity. When adding it to semi-finished products (puree, paste, powder) creates the preconditions for the production of dietary, food additives and products with multifunctional properties [70].

Pectin-containing powders are obtained from apple, carrot pomace and beet pulp. Raw materials are processed in a solution of food grade acids. After pressing the pomace or pulp is dried at a temperature not exceeding 90 ° C and crushed (table 3.22) [67, 68].

Pectin-containing powders are used as an additive in various foods 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.

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

Dry pectin-containing mixtures "Pektosan" obtained 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 at the Dnipropetrovsk Medical Academy have shown that heavy metals bind at the level of the gastrointestinal tract and reduce the amount of xenobiotics that pass through the body and are fixed in the tissues when using "Pektosan" mixture based on beet pectin powder. 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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PERTSEVOY Fedir

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Адреса виробництва:
61000 Харків Ващенковський в'їзд 16