Innovative technological aspects of secondary raw materials processing in juices production

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Abstract. The agricultural sector of the economy is a waste-intensive industry. Production of the basic agricultural product involves a big amount of waste. The output of the target product, as a rule, makes up 15–30% of the full amount of the initial resources. The other part that contains a significant number of valuable compounds is not used in this process and turns into the so-called production wastes, which can become secondary raw materials for an extra product manufacturing. The vast amount of secondary raw materials is created in food and processing industries of agricultural Complex (AC). At the same time, only 50% is used efficiently. This fact proves the relevance of the secondary resources processing problem. The production of apple juice creates 20–30% of wastes that are the industrial source of pectin. As a rule, pectin is extracted from the runoff of late ripening period apples. The objects of this research are the industrial apples cultivars grown in Krasnodar region. The article provides the comparative research results of fractional content of pectin substances in apples with different ripening periods. It defines analytical characteristics of apple pectin extracted from different raw materials. The study states the innovation evaluation criteria for developed technologies. It shows the reasonability of summer period apples processing for production of pectin-containing products and their competitiveness.

1. Introduction
High rates of scientific and technological development, conditions of instability and changing environment make companies and organizations introduce innovations in production and servicing in order to preserve or improve their position in the market. Innovations imply, first of all, the innovative approach, innovative processes, and innovative activity.

In the academic literature there is a wide range of approaches to defining the terms “innovation” and “innovative activity”. In its direct meaning “innovation” means “introduction of something new”.

Joseph Shumpeter is considered to be the founder of the innovation theory. His works are traditionally viewed as the “starting point” in the row of the following scientific works on the problem of innovations [1]. For a new idea to be developed into a new technology and a new product, it has to possess some certain criteria: scientific and technological novelty, practical applicability and commercial feasibility.

The given criteria mean that a new idea in itself, no matter how well it has been described, formalized and presented in tables and schemes, is not yet an innovation if it is not applied in practically used products, services or processes. That is why the commercialization of innovations is closely related to the stages of the innovation process and has the following basic aspects:

1) technological (T), when a new technology acts as the first innovative result of scientific and
practical activity;

2) applied (A), when application of a new technology in new products and services acts as the second result of innovation process.

Therefore, innovative technological aspects of processing secondary raw materials in juices production, in our opinion, must be influenced by the development of the technology of their usage in food product that would meet the requirements of the contemporary food market.

It is known that the most promising trend of agricultural complex in the developed countries involves the increase of production volume of agricultural products, the improvement of their quality, the increase of nutritional and biological value of processing products, the expansion and the improvement of the product range. All this defines the type of innovations in this industry.

The focus of innovations is also influenced by the present increase in the intensification and chemicalization of agriculture, leading to high accumulation of dangerous chemical substances in the environment. On getting into the ecosystem, poisonous and ecologically dangerous substances do not disappear but, being accumulated by plants from the environment, where they have come to with the emissions of different food and other production plants, and having entered the biological cycle, these substances move up the food chain. It is known that 70% of alien harmful substances and toxins are absorbed from food.

So, one of the food problem aspects, on the international level, is the lack of food products that possess detoxication qualities, which, in its turn, leads to the growing number of cancer, heart diseases and diabetes. That is why, integrated use of agricultural raw materials makes it reasonable to carry out research and create new competitive products meeting the requirements of quality and safety, and containing pectin substances [2, 3].

There is a big number of dominating producers on the world pectin market; many of them have production sites in different countries and regions. This production is labor and cost consuming since it requires a definite level of technology and knowledge. That’s why now the biggest pectin producers are the developed counties, while raw materials come from the developing ones.

Europe is the leading producer of pectin; the share of Denmark comprises about one third of the world production. The citric (~70%) and apple (~25%) peels are the basic sources of pectin. Apple pectin is produced mostly in Europe, while citric pectin is more popular in Latin America.

It is surprising, but nowadays there are 7500 sorts of apples in the world. Apple gardens occupy incredibly vast territories of 5 million hectares, which means that almost every second tree is an apple tree [4]. However, in our opinion, apple raw materials functional qualities are not enough considered.

This fact brings out a necessity to study apples from the perspective of their use as a basis for functional products needed to establish rational eating patterns. Considering the world tendency toward healthy eating habits, food market of pectin-containing products shows a stable growth.

Most of the researchers carry out studies not only of chemical content of apples but also of analytical characteristics of contained pectin substances [5]. The major object of the study is the extract of the late ripening period apples. For example, A. Baron, R Massiot and others studied the activity of cell ferments of apples and their influence on juice output [5, 6]. Similar studies were done by the French scientists C. Grassin and P. Fauquembergue [7].

The works by H.A. Schols, C. Renard, A.G.J. Voragen and W. Pilnik [8] provide the results of studying the structure and chemical changes of apple pectin molecule without their relation to the apples cultivars and ripening period. Patrice Pellerin, Thierry Doco and others [9] continued the research in the same direction, having studied changes of polygalacturonic compound in fruit raw material, including apples.

Juices production uses the mixture of apples. However, depending on the season, they process different ripening period cultivars. So, this factor has to be taken into account.

It is known that fractional content of pectin substances in plant raw materials, as a rule, is presented by hydro- and proto pectins which are located in different cell parts [4, 7]. The ratio between these fractions, in our view, defines the production importance of the raw material and the conditions of pectin substances extraction [10, 11].
In this way, the results of research of pectin substances fractional composition and analytical characteristics are the foundation for the development of innovative technologies of apple raw material complex processing.

2. Materials and methods

The experimental area chosen by the authors is the south of Russia, Krasnodar Region, to be exact.

Krasnodar Region is situated in the south of Russia, in the south-western part of North Caucasus. This geographical location defines special features in the chemical composition of the vegetable raw material. Apart from this, this region traditionally has industrial plantings of apples. Introduced sorts prevail among these plantings.

We have chosen industrial sorts of apples as the objects of the study: White Transparent, Borovinka, Valentine, Grimes Golden, Rouge Grieve, Memory of Esaul, Ranger, Rennet Landsberg, Quinte, Cuff Apples, Melba, Red Melba, Pearmain Winter Golden, Prima, Glory to the Winners, Stark Andrew, Süislep, Welsey, Airlie.

The quantification method of pectin substances in vegetable raw material is based on the extraction of hydropectin and protopectin and its solubilization. The basis of hydropectin and protopectin research is calcium-pectin method and sedimentation in alcohols. Apart from this, the authors studied the content of carboxylic groups (free and esterified), methoxy and acetyl groups and the degree of esterification in pectin substances using conductometric method, based on changing conductivity of hydropectin and protopectin.

3. Results and discussion

To assess the relevance of the studied apples cultivars, especially of the summer ripening period, we have studied their fractional composition of pectin substances: protopectin (PP) and hydropectin (HP).

These fractions of pectin substances (PS) fulfill different functions in plant tissue and, depending on biochemical processes, change their state.

Experimental data on the protopectin and hydropectin content in the researched cultivars of late ripening period apples is shown in Figures 1 and 2.

The results of the study showed that the White Transparent contains the biggest amount of hydropectin (0.69%). The lowest number is observed in Melba sort (0.17%). The rest of the sorts contain about 0.2–0.6%. The highest number of protopectin is contained in Stark Andrew (2%) and the lowest – in Borovinka (0.8%). The general content of pectin substances in these sorts varies from 1 to 1.8%.

For the purpose of evaluating the industrial importance of early ripening period apples some additional comparative analysis of late period apples has been done. Experimental data on fractional content of pectin substances in the studies autumn sorts is shown in Figures 3 and 4.

![Figure 1. Content of hydropectin in studied apples of summer ripening period, %](image1.png)

![Figure 2. Content of protopectin in studied apples of summer ripening period, %](image2.png)
The results of the research show the biggest amount of hydropectin in Grimes Golden (0.78%) and the least amount – in Prima (0.02%). In other types the hydropectin content varies between 0.05 – 0.6%. A new Valentine cultivar has the biggest content of protopectin (4.05%), the smallest content is discovered in Rouge Grieve (1.0%). The general content of pectin substances in the given apples cultivars fluctuates from 2 to 3.5.

Analyzing the obtained data, one can draw a conclusion that there is no dramatic difference in pectin substances content between summer and autumn types of apples. This fact enables us to consider summer types of apples as a pectin-containing raw material [12].

However, apart from mass pectin fraction, an important property of pectin-containing raw material is the ratio between protopectin (PP) and hydropectin (HP). This ratio implies the difference of pectin extraction technological methods.

Table 1 shows that almost all summer cultivars of apples studied have a lower PP and HP ratio (4.24) compared to the autumn cultivars.

| Group | INDEX PP/HP | Types |
|-------|-------------|-------|
| I     | > 13        | Valentine, Pearmain Winter Golden, Prima, Rennet Landsberg, Welsey, Airlie |
| II    | 6 – 13      | Grimes Golden, Glory to the Winners, Melba, Stark Andrew White Transparent, Borovinka, Borovinka Sergeev, Quinte, Cuff |
| III   | < 6         | Apples, Red Melba, Ranger, Suislep, Rouge Grieve, Memory of Esaul |

The commercial relevance of the pectin-containing raw material is assessed not only according to pectin substances content, but also according to their analytical characteristics which, in their turn, define the target use of extracted pectin.

It is known that their ability to form jell and complex structures affect the use of pectin in food industry for the production of food with curative and protective properties and dietary supplements with different consistency.

Jelly forming depends, primarily, on the esterification degree of pectin molecule and on the content of functional groups – methoxyl and acetyl compounds [2, 10, 13].

Analysis of the received data shows that the highest content of methoxyl compound is observed in early-period apples – Suislep (13.8%) and in autumn period cultivar – Airlie (7.7%). The least content is discovered in Melba (5%) and Valentine (1.1%) cultivars.
The studied apple cultivars do not differ in terms of acetyl compound. The quantity number of acetyl groups fluctuates from 0.1 to 0.2%. Summer period apples contain more acetyl groups than autumn types do. Such content of acetyl compound leads to the decrease in jelly density.

This, in its turn, allows making a conclusion about the higher ability of pectin substances of summer period apples to form jelly in comparison to autumn period apple cultivars. The drawn conclusions coincide with the academic literature data.

One of the most important properties of pectin substances is their complex forming ability based on interaction of pectin molecule with ions of heavy and radioactive metals.

This property enables us to recommend pectin as a nutrition component for people who live in the environment polluted with radionuclide and who contact with heavy metals.

Complex forming properties of pectin substances depend on free carboxylic groups i.e., on the esterification of carboxylic groups with methanol.

The analysis of the provided data showed that the content of free carboxylic groups is higher in pectin of autumn apples cultivars. The biggest number is discovered in Valentine and Grimes Golden (4%) and the smallest – in Winter Golden Pearmain, Rennet of Landsberg and Airlie (2%). In the rest of the cultivars the content of free carboxylic groups is about 3%.

Pectins of summer period apples have approximately equal content of free carboxylic groups (1%). According to the degree of esterification almost all pectin’s of the studied apple cultivars should be referred to highly esterified ones. This coincides with the data on the free carboxylic groups’ content.

The obtained experimental data on the analytical properties of the studied pectin substances allow characterizing them as pectin substances with the index that meets the requirements of the food industries.

An index, reflecting the content of polygalacturonic compound, is also very important for organizing production of functional pectin-containing food.

We have done some extra research on defining the quantity of that index in pectin of the studied cultivars of apples.

The amount of polygalacturonic compound in pomace of early ripening period apples varies from 39 to 59% (without additional clearing)

The amount of polygalacturonic compound in the pomace of late ripening period apples changes from 45 to 65% and it is a little higher than in summer ones. This evidence makes us suggest that summer types are almost similar to autumn types in terms of content and analytical characteristics of pectin substances.

The industrial types of apples chosen for the research: White Transparent, Borovinka, Valentine, Grimes Golden, Rouge Grieve, Memory of Esaul, Ranger, Rennet Landsberg, Quinte, Cuff Apples, Melba, Red Melba, Pearmain Winter Golden, Prima, Glory to the Winners, Stark Andrew, Suislep, Welsey, Airlie demonstrated industrial applicability as a raw material for pectin production.

The results of studying fractional content of pectin substance in summer (early) ripening period apples showed that White Transparent stands out because of the biggest amount of hydropectin (0.69%), and Melba – because of the smallest (0.17%). The amount of hydropectin in other cultivars varies from 0.2 to 0.6%. The biggest amount of protopectin is observed in Stark Andrew (2%) and the smallest – in Borovinka (0.8%). A general amount of pectin substances in these types of apples varies from 1.0 to 1.8%.

The biggest amount of hydro pectin in autumn (late) ripening period cultivars has been discovered in Grimes Golden (0.76%) and the smallest – in Prima (0.02%). The new Valentine cultivar is distinguished with the biggest amount of protopectin (4.05%) and Rouge Grieve – with the smallest (1.0%). The general content of pectin substances varies from 3.0 to 3.5%.

According to the ratio between protopectin and hydrolyzed pectin all summer apple cultivars demonstrate lower ratio PP/HP (4.24%) compared to that of autumn sorts. This dictates the use of different modes of pectin substances extraction. For example, the process of hydrolysis extraction of pectin substances from summer period apples must be “milder” than that from autumn period apple.
In terms of analytical characteristics of pectin substances, summer and autumn apple cultivars do not really differ. They all are highly esterified. The content of polygalacturonic component fluctuates (without additional removing of ballast substances) between 39–65%, depending on the apple cultivar.

So, the results of the research prove the reasonability of developing technologies for obtaining pectin and pectin-containing substances from the studied summer types of apples.

4. Conclusion
1. The results of the research showed promise for using summer pomace waste as a raw source of pectin substances for the production of specialized foods having detoxification properties.
2. It has been discovered that in terms of esterification, content of methoxyl, acetyl and polygalacturonic compounds in summer period apples have no significant differences comparing to standard requirements to apple pectin.
3. The innovativeness of a complex summer apples processing technology results from technological and applied aspects – receiving pectin products and pectin-containing foods.

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