FOOD TECHNOLOGY PROGRESSIVE SOLUTIONS

Collective monograph

Edited by
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ABSTRACT

The monograph "**Food Technology Progressive Solutions**" is dedicated to finding effective solutions for reducing food resource losses, their rational use, analysis, and the implementation of innovative technologies in the food industry aimed at improving the quality and preserving the beneficial properties of food products. The book consists of nine chapters, each covering different aspects of food technologies and offering promising solutions for the modern food industry.

Strategies for reducing postharvest losses of vegetables through integral assessment of antioxidant status.

The application of edible coatings with antioxidant properties is an effective strategy for preserving vegetable quality during storage. To make an informed choice of the concentration of exogenous antioxidants in food coatings, it is recommended to evaluate the antioxidant status of the product. A method for the integral assessment of the antioxidant status of vegetables using the analytical hierarchy process has been developed. An example of this integral assessment is provided for three varieties of asparagus of different colors.

The advantages of using sublimation for preserving the antioxidant properties of cranberries.

The benefits of using sublimation for preserving cranberry antioxidant properties have been explored. Sublimation drying has emerged as the most efficient and innovative method, ensuring the retention of cranberry antioxidants. Following the sublimation cycle, the material's final moisture content is only 2–5 % of the initial amount, guaranteeing maximum preservation of beneficial properties and high-quality product production.

Analysis of the hypotheses of milk fat phase dispersion and structural features of homogenizers.

A detailed analysis of the structural features of homogenizers and their impact on the dispersity of the milk fat phase, which affects the quality of dairy products, is presented. Analysis of methods of intensifying the dispergating process of milk emulsions resulted into distinguishing prospective ways to increase energy efficiency of homogenizers and designs with the biggest potential for diminishing energy consumption.

Qualimetric assessment and features of quality formation for cultivated mushrooms in accordance with the methods of further processing.

The study examines factors influencing the quality of harvested mushrooms from the *Calocybe*, *Cyclocybe*, and *Pleurotus* genera, as well as methods for assessing raw material quality for processing. It establishes parameters for comprehensive

quality assessment, including individual and group indicators, evaluates morphological changes during mushroom maturation, and investigates the nutritional value of mushrooms.

Technology of multilayer and glazed fruit and vegetable chips.

A technology has been developed for producing multilayered and glazed fruit and vegetable chips with enhanced nutritional composition. This method preserves the taste, color, and nutrients of the raw materials, while chocolate helps balance the nutritional value. Additionally, the incorporation of powders from freeze-dried plants enriches the chips with vitamins and minerals, providing them with new flavors and colors.

Improving the quality of dairy sauces by using condensed low-lactose milk whey.

This chapter of the monograph presents research on using fermented mashed pumpkin pulp with high pectin content and condensed low-lactose milk whey in emulsion sauces similar to mayonnaise. The study establishes rational oil emulsification parameters and examines model samples with varying ratios of fermented mashed pumpkin pulp and condensed low-lactose milk whey.

Crafting fermented pepper-based hot sauces.

This study examines craft hot sauce technology, organizing theoretical and methodological advancements, and offering insights into production methods for the restaurant industry. It delves into the principles, features, and practical experiences of craft hot sauce production, emphasizing the benefits of employing innovative technologies in this sector.

Biological activity of phenolic compounds of oats depending on the technology of its use in feeding geese.

The study compares the effects of aqueous extracts from sowing oats and oats on the development of geese and the nutritional value of their meat. Results show that adding oats and alfalfa to the geese's diet boosts meat nutrients. These benefits persist even during prolonged low-temperature storage, improving the meat's nutritional value.

Justification of the technology for the use of phyllophora (zernov field) carrageenan as a regulator of the consistency of food products.

The results of theoretical and experimental studies, as well as progressive solutions regarding the utilization of the phytocolloid carrageenan extracted from the Black Sea red algae *Phyllophora Brody* as a food consistency regulator, are presented. The technological aspects of employing carrageenan from the Black Sea red algae *Phyllophora Brody* are also substantiated.

Keywords

Postharvest loss and waste, storage, vegetables, antioxidants, antioxidant system, edible coatings, hierarchy analysis method, cranberry, drying technology,

sublimation, nutritional value, polyphenolic compounds, milk homogenization, hydrodynamic factors of emulsions dispersion, design analysis of homogenizers, principle of homogenizer action, classification of homogenizers, Calocybe, Cyclocybe, Pleurotus, pioppino, gold oyster mushroom, lung oyster mushroom, milky mushroom, quality, cultivation, fruit chips, vegetable chips, multilayer chips, glazed chips, healthy chips, properties of chips, sauce, emulsification, mayonnaise, egg-free sauce, milk whey, lactose intolerance, lactose malabsorption, craft production, hot pepper, fermentation, biological value, functional properties, organoleptic indicators, sowing oats, avenanthramides, goose meat, end products of lipoperoxidation, vitamin E, β-carotene, fatty acids, amino acids, carrageenan, phytocolloid, consistency regulator, extraction, rheological properties, physical and chemical properties.

CIRCLE OF READERS AND SCOPE OF APPLICATION

The collective monograph "Food Technology Progressive Solutions" serves as a valuable resource for scientists, food engineers, and professionals in the food industry seeking to implement innovative technological solutions for enhancing the quality and efficiency of food production. The scope of application of the research results presented in the monograph includes:

– *modernizations of technologies in the food industry*: scientists, food engineers, and professionals in the food industry can apply the findings to implement innovative technological solutions aimed at enhancing the quality and efficiency of food production;

– *postharvest loss reduction*: strategies for reducing postharvest losses of vegetables through antioxidant status assessment can be applied by agricultural professionals and food processors to preserve vegetable quality during storage;

– *food preservation technologies*: techniques such as sublimation drying for preserving cranberry antioxidants offer practical applications in food preservation and processing industries;

– *dairy product quality improvement*: insights into homogenizer features and their impact on dairy product quality can guide dairy processors in optimizing energy efficiency and reducing energy consumption while maintaining product quality;

– *mushroom cultivation and quality assessment*: mushroom growers and processors can utilize qualimetric assessment methods to ensure the quality of cultivated mushrooms and optimize processing methods;

– *snack food production*: the development of multilayered and glazed fruit and vegetable chips offers new opportunities for snack food manufacturers to produce nutritious and flavorful snack options;

– *sauce manufacturing*: the research on improving dairy sauce quality with condensed low-lactose milk whey provides valuable information for sauce manufacturers seeking to enhance product quality and nutritional value;

– *hot sauce production*: analysis of craft hot sauce technology and innovative solutions provides insights for hot sauce producers to improve production processes and product quality;

– *poultry farming and meat production*: the study on the biological activity of oats phenolic compounds in goose feed can be applied by poultry farmers to optimize feed formulations and improve meat quality;

– *food texture modification*: the research on using phyllophora carrageenan as a food consistency regulator offers potential applications in food texture modification and product development for food manufacturers.

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INTRODUCTION

Focus on food system challenges

Olesia Priss

In today's world, food systems are facing unprecedented challenges. The fragility of these systems is becoming increasingly evident as they are continuously strained by numerous factors, including climate change, population growth, resource shortages, and economic instability. One of the most pressing issues is the increase in food resource loss and waste, which not only exacerbates environmental degradation but also undermines food security. The monograph «Progressive Solutions in Food Technologies» addresses these critical challenges, presenting innovative technological solutions aimed at enhancing the resilience and sustainability of food systems.

Focusing on reducing food resource losses, promoting the rational use of secondary resources, enhancing the biological value of food products, and implementing advanced technologies in the food industry, this monograph highlights technological solutions designed to strengthen global food systems. Covering all aspects of food systems, from solutions for growing raw food materials, post-harvest handling, processing raw materials into final products to consumption, these technologies offer comprehensive solutions to current and future problems.

Food losses and waste are serious issues for global food systems. Post-harvest losses, inefficient processing methods, and improper storage are primary factors in the degradation of food quality and depletion of valuable resources. The monograph emphasizes strategies to mitigate these problems, including the use of advanced storage methods for fruit, vegetable, and mushroom products that account for he potential of the raw materials. For example, assessing the antioxidant status of vegetables and applying edible coatings with antioxidant properties can significantly extend shelf life and maintain quality, thereby reducing waste. Modern methods of optimizing post-harvest procedures and storing mushrooms have identified critical storage periods based on processing directions.

Another important aspect discussed in the monograph is the use of secondary resources in food production. The food industry generates a significant amount of

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by-products, which, if not properly managed, can contribute to environmental pollution. However, these secondary resources have enormous potential for reuse in various applications. The monograph explores innovative uses of condensed low-lactose whey and fermented pumpkin pulp puree in dairy and sauce products. These ingredients not only enhance the nutritional profile of the final products but also represent a sustainable approach to managing food by-products. This approach allows for the efficient use of secondary resources while meeting diverse dietary needs, including lactose intolerance. Such innovations highlight the potential for creating high-quality, nutritious food products through the rational use of food by-products.

Focusing on improving the energy efficiency of the milk homogenization process, the monograph proposes homogenizer designs with the greatest potential for reducing energy consumption.

Enhancing the biological value of food raw materials is crucial for ensuring that food products are both nutritious and beneficial for health. The monograph presents several technological solutions aimed at increasing the nutritional value of food products. One study address feeding geese with extracts from oats and alfalfa to increase the biological value of meat and its stability during storage. Adding these extracts to the diet not only increased meat yield but also boosted protein content by 5.0 %, which is particularly important in the context of growing protein deficiency. The importance of mushrooms in the modern diet is also highlighted due to their functional properties. The monograph examines the expansion of the assortment and quality of cultivated mushrooms, establishing parameters for comprehensive quality assessment, as well as methods for evaluating and preserving their nutritional value.

Preserving the nutritional and biologically active compounds in food products is essential for maintaining their health benefits. For example, developing multilayer and glazed fruit and vegetable chips demonstrates how combining traditional ingredients with innovative processing technologies can create snacks rich in vitamins and minerals. Adding freeze-dried plant powders to these chips further enriches their nutritional value, providing consumers with healthier snack options. The monograph discusses advanced preservation methods, such as freeze-drying, which has proven effective in maintaining the antioxidant properties of cranberries. It also analyzes the technologies and biological value of new sauce products based on fermented hot peppers.

Improving the texture and stability of food products is another focus of the monograph. The use of Phyllophora carrageenan, a phytocolloid derived from Black Sea red algae, as a food consistency regulator exemplifies this approach. By utilizing the unique properties of natural ingredients, food technologists can enhance

the texture and stability of food products, meeting consumer expectations while promoting sustainability.

We hope that the theoretical and practical aspects of technological approaches to process and system improvements proposed in this monograph will be useful for food industry professionals. Additionally, we aim to inspire researchers to address the complex challenges facing modern food systems, ensuring a more stable, nutritious, and sustainable food supply for future generations.

CHAPTER 1

Strategies for reducing postharvest losses of vegetables through integral assessment of antioxidant status

Olesia Priss
Szymon Glowacki

Abstract

The global food system is facing a challenge due to high total food losses and waste, with the problem exacerbated by unpredictable events like pandemics and conflicts. The loss of fruit and vegetable products, particularly during storage, becomes a critical issue demanding attention and technological advancement. Reducing such losses will not only ensure a sustainable food resource, but also contribute to the reduction of greenhouse gas emissions and efficient use of resources. Long-term and efficient storage of vegetable products is, however, a difficult task, since many vegetables have a short production and marketing cycle and perish quickly. After separation from the mother plant, vegetables are exposed to various stress factors that lead to the generation of reactive oxygen species, which are harmful to cells, but also act as signal messengers at low concentrations. The plant's antioxidant system, comprising both low-molecular and high-molecular antioxidants, plays a crucial role in regulating the level of reactive oxygen species (ROS) and maintaining redox homeostasis. A well-functioning antioxidant system is important for preserving the quality of vegetables during storage and preventing postharvest disorders. The use of edible coatings with antioxidant properties is an effective strategy for maintaining the quality of vegetables during storage. However, it is important to note that high doses of antioxidants can potentially have a toxic effect, and their efficacy may vary depending on the concentration and type of vegetables. To strengthen the endogenous antioxidant system, it's crucial to determine the concentrations of exogenous antioxidants that align with the endogenous pool of antioxidants in plant tissues and ensure the maintenance of the antioxidant status and the preservation of the quality of vegetables during the postharvest period. To assess the antioxidant status, we propose employing the method of analyzing hierarchies (AHP). The main drawback of AHP is its susceptibility to subjective evaluation judgments. This subjectivity

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can be eliminated by relying on experimental or analytical information about the quantitative indicators of the chemical composition, correlations between the components of the antioxidant system and with markers of oxidative stress. This study introduces the method of integral assessment of the antioxidant status of vegetables using the hierarchy analysis method. The integral assessment was conducted on three varieties of asparagus with different colors. We suggest adjusting the concentration of antioxidants in the composition of edible coatings based on the determined antioxidant status of vegetables. This approach ensures the prevention of product losses during an extended shelf life.

Keywords

Postharvest loss and waste, storage, vegetables, antioxidants, antioxidant system, edible coatings, hierarchy analysis method.

1.1 Introduction

To date, the global food system exhibits a considerable fragility. Russia's war in Ukraine has notably exacerbated the negative trends within the current state of the world food system, leading to breaches in guaranteeing obligations to ensure food security [1]. Undoubtedly, the consequences of Russian aggression, such as the blockade of Ukrainian seaports (which serve as the primary logistical route for grain export), the looting of crops in occupied territories, the destruction of arable land in combat zones, and the demolition of the Kakhovka Dam, will have lasting repercussions not only for Ukraine's food system but also for global food security. The food system includes all stages from the production (growing) of food raw materials to the consumption of ready-made food. Mandatory links of the food system are cultivation, harvesting, postharvest processing, pre-processing storage, raw material transformation into finished products, storage of the finished products, their delivery to distribution centers, distribution, and sale to the final consumer. Naturally, transportation involving loading and unloading occurs between these stages, thus leading to losses of food raw materials and products at each link of the food chain.

Food losses and waste are symptomatic of the inefficient functioning of the food system. After all, the production of food requires significant resources, such as water, soil, energy and fertilizers. When part of the products turns into waste, these resources are irretrievably lost and become an additional source of greenhouse gas emissions. This leads to the use of non-renewable resources to produce food that will not be used (for example, about 25 % of the water resources used by

agriculture annually and 23 % of arable land, which generates about 8 % of annual global greenhouse gas emissions) [2]. Concerned with the problem of food loss reduction, Food and Agriculture Organization (FAO) introduced the global initiatives "Safe food" and "Technical Platform on the Measurement and Reduction of Food Loss and Waste". Fruits and vegetables occupy leading positions in the list of food losses and waste (40–50 % of their total production). Reducing the loss of fruit and vegetable products thus is not only vital for sustainable food resources but also aids in mitigating the environmental impact by curbing greenhouse gas emissions and promoting more efficient use of valuable resources within the food industry. This endeavor necessitates involvement across the entire food chain, from agricultural producers to consumers, in order to effectively reduce postharvest losses of vegetables.

According to the analysis of the food waste market, in 2022 the fruit and vegetable segment dominated the market and accounted for 20.3 % of the total revenue share. This dominance is attributed to factors such as improper handling, storage, processing, and cultivation practices of these products [3]. Losses of fruit and vegetable products occur at all stages, including cultivation, harvesting, processing, storage, logistics and distribution to consumers. The later the losses occur, the more damage these losses will cause to the global food system. It is known that in countries with imperfect collection, processing, and storage technologies, the greatest losses occur at the initial stages. In countries with high-tech systems of agriculture with a well-developed cold chain, the largest share of products is thrown away at the stage of retail trade and consumption of products. In both cases, a certain share of fruit and vegetable products is lost at the stage of storage. One of the solutions to this problem is the improvement of storage technologies and methods that allow to extend the shelf life of vegetables and reduce their losses.

On the other hand, according to the FAO recommendations, the share of fruit and vegetable products in the population's diet should constantly increase with the transition to sustainable consumption patterns [4]. Fruits and vegetables contribute to health by providing essential phytonutrients such as phenolic compounds, carotenoids, vitamins, mineral compounds including potassium, calcium and magnesium, iron, iodine, zinc and fiber. They are important for the prevention of "hidden hunger". The spectrum of biologically active compounds is, however, a feature specific to species and variety. Bioactive substances in fruits and vegetables with redox modulator properties may also mitigate the risk of chronic diseases such as diabetes, vision disorders, as well as asthma and viral infections. Numerous studies have shown a direct correlation between the consumption of vegetables and the reduction of cardiovascular diseases (Mediterranean, flexitarian diets). Vegetables contain more protein and fiber and less carbohydrates than fruits.

In general, FAO recommends consuming at least 400 g (5 portions of 80 g) of fruits and vegetables per day. It is believed that at least three portions (240 g/day) should consist of vegetables [5]. The general concept is that including various vegetables in the diet is a key element for a balanced diet. Hence, significant attention should be devoted to addressing the issue of reducing vegetable losses, given their importance as a valuable food resource.

1.2 Problems of reducing losses during storage of vegetables

Effectively storing vegetable products poses a significant challenge due to several issues. The production of vegetables is seasonal and their production and marketing cycle is quite short. In general, for many vegetable crops, this cycle lasts only for 2–3 months. Some cruciferous vegetables – cauliflower, kohlrabi, broccoli can be stored for only 2–3 weeks. However, there are very perishable vegetables (for example, leafy and fruit vegetables), which shelf life is measured not even in weeks, but only in days. This leads to oversaturation of the market during the production season followed by further large losses and waste. Almost all types of vegetables, with the exception of some varieties of pumpkins, possess thin covering tissues that are susceptible to mechanical damage during the loading and unloading processes, leading to potential injuries. These damages, as a rule, become evident already in storage, which leads to increased losses. After all, injured tissues become an easy target for pathogens that multiply quickly and attack intact vegetables. High free water content in tissues can cause wilting and weight loss as a result of natural shedding. Vegetables with low turgor become more vulnerable to pathogens, quickly undergo microbiological spoilage and lose their quality.

The preservation of vegetables is affected by a combination of various factors, the main of which are: botanical and biological properties of raw materials, climatic and soil growing conditions, agrotechnical measures during the growing season, conditions of collection, transportation, postharvest processing and storage.

The main purpose of storage (long-term or short-term) of fruit and vegetable products is to maintain the initial quality of products during a certain period. After harvesting, fresh vegetables remain living biological objects and continue metabolic activity. Temperature, humidity, lighting affect the life processes of the fruit almost as much as before separation from the mother plant. The speed of metabolic reactions, including respiration, slows down by 2...3 times with a decrease in temperature for every 10 °C and, accordingly, accelerates with its increase. Respiration is considered the main physiological process of the postharvest period, which performs certain

functions in the plant organism. First of all, the energy released during the oxidation of biological substrates (acids, sugars) is transformed into convertible forms of cellular energy and is used to maintain vital processes. When biological substrates undergo oxidation, they produce metabolites that are utilized in various biosynthetic pathways. Due to metabolic processes and transpiration, moisture loss occurs. In the postharvest period, as photosynthesis ceases, replenishing reserve substances and moisture becomes impossible. Accumulated substances are constantly spent on maintaining metabolism, which leads to the loss of nutritional value, decline in organoleptic indicators, weight loss, and a decrease in quality. Therefore, quality losses of fruit and vegetable products during storage is a natural and irreversible process. Since it is already impossible to improve the quality of vegetables in the postharvest period, the main task is to maintain the proper quality of products for as long as possible.

Primarily, normal metabolism is inhibited by altering physical factors such as temperature, relative humidity, or gas composition within the storage atmosphere. The maximal preservation of food, retention of vitamin value, maintenance of quality parameters, and ensuring safety of fruit raw materials, along with minimizing production losses, can only be achieved through the application of artificial refrigeration. It is known that a decrease in storage temperature is directly correlated with the intensity of respiration, production of ethylene, inhibition of metabolism, as a result of which the shelf life is extended. Different types and varieties of vegetables require different modes not only for storage, but also for pre-cooling and subsequent heating after storage. The difficulty of choosing the optimal storage regimes also lies in the fact that the recommendations developed for products grown in different regions and agro-climatic conditions may differ.

Traditional methods of vegetables storage, based on artificial refrigeration, fail to comprehensively address the challenge of long-term storage and loss prevention. Low positive temperatures only slow down, but do not stop, oxidation-reduction processes and the development of microflora, and therefore, during vegetables storage in ordinary refrigerating chambers a relatively high rate of aging processes and significant losses from microbiological diseases and physiological disorders are noted. Control of relative air humidity along with the temperature control is important for reducing mass loss. Increase in relative humidity in storage leads to stimulation of the development of fungal pathogens. As a supplement to the influence of temperature and relative air humidity, other technological methods can be used during storage. Supplementing the cold chain with a regulated storage atmosphere further slows postharvest metabolism and extends shelf life. However, controlled atmosphere storage can be beneficial, ineffective, or even harmful depending on the type of product. There is great variability in the tolerance of fruit and vegetable products to a regulated

atmosphere, and genetic factors determine the product's ability to withstand stress from changes in the composition of the atmosphere [6]. In addition, there are questions about the environmental friendliness of this method of storage. Nowadays, it is important to develop and implement vegetable storage technologies that not only reduce losses, but also minimize the negative impact on the environment.

In any case, preventing the natural process of aging and deterioration of fruits and vegetables during storage is a fundamental challenge from a technical point of view.

1.3 Endogenous mechanisms of maintaining normal metabolism in the postharvest period

After separation from the mother plant, vegetables undergo various stress factors during postharvest processing and storage, including mechanical shocks and damage, compromise of covering tissue integrity, fluctuations and changes in temperature regimes, and conditions leading to increased water loss. These stress factors cause intensive generation of partially reduced reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), superoxide anion ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2), hydroxyl radical ($OH^{\bullet}$), peroxynitrite ($ONOO^-$). Free radicals and other oxygen derivatives are inevitable side products of biological redox reactions, as well as a consequence of aerobic metabolism in plants [7]. They are formed in the process of respiration, photosynthesis, oxidation of fatty acids. Depending on their concentration in the cell, ROS can be both harmful and beneficial. At high concentrations, ROS can damage various types of biomolecules, whereas at low or moderate concentrations, they serve as messengers in intracellular signaling pathways [8]. ROS signaling is important during plant vegetation. However, in the postharvest period, excess ROS generation leads to the loss of the body's ability to maintain cellular redox homeostasis. The duration of reactive oxygen species (ROS) activity within tissues is determined by the antioxidant system or the antioxidant status of the cell (AOS), comprising a collection of protective mechanisms within cells, tissues, organs, and systems aimed at preserving and maintaining homeostasis. Endogenous antioxidants help maintain a low steady-state level of ROS, thereby preventing oxidative damage during the postharvest period.

The antioxidant system of plant tissues is formed basing on the complex of non-enzymatic (low-molecular) and enzymatic (high-molecular) antioxidants. Low-molecular-weight antioxidants (AO) are most important in the early stages of activation of increased ROS formation. These substances donate their hydrogen atom, transform free radicals into stable molecules and prevent the development of a chain reaction of peroxide oxidation. However, with time their number is quickly exhausted and

depends on the activity of enzymes that restore them. Low-molecular non-enzymatic antioxidants are present in all plant organs and include ascorbic acid, carotenoids, phenolic compounds, glutathione, etc. [8].

Ascorbic acid (AA) has several antioxidant properties: it acts as a primary substrate in the cyclic pathway of enzymatic detoxification of ROS (H_2O_2), has the ability to directly neutralize superoxide radicals, singlet oxygen, and hydroxyl radicals. AA also serves as a cofactor for many enzymes and promotes ROS detoxification. In addition, the endogenous level of AA plays an important role in the regulation of aging processes and protection against pathogens [9]. Certain vegetables contain large amounts of AA. However, AA content tends to decrease during storage. Losses of AA during storage of plant products are associated with enzymatic metabolism and oxidation by ascorbate oxidase localized in the cell wall. Plant AA is also oxidized by peroxidase.

Plant carotenoids (CAR) belong to the group of lipophilic antioxidants and are able to neutralize various forms of ROS. Carotenoids are the main utilizers of singlet oxygen [10]. They protect cellular structures from the influence of ROS, not only by extinguishing singlet oxygen, but also prevent peroxidation of lipid components of cell membranes by neutralizing peroxide radicals and interrupting the chain reactions of free radical oxidation of unsaturated carboxylic acids. The ability of carotenoids to utilize excess ROS and prevent or minimize the formation of triplet chlorophyll is defined by the specificity of their chemical structure. CARs have a chain of isoprene residues with multiple double bonds that allow easy absorption of energy from excited molecules and dissipation of excess energy as heat. Carotenoids also serve as precursors of signaling molecules that influence the development of plant responses to biotic and abiotic stresses [10].

Phenolic compounds (PC) are various secondary metabolites (flavonoids, tannins, hydrocinnamic esters and lignin) that have antioxidant properties. Polyphenols contain an aromatic ring with several hydroxyl groups, which determines their biological activity, including antioxidant action. In terms of antioxidant activity, phenolic substances are not less efficient than ascorbic acid or α-tocopherol. Polyphenols can chelate metal ions with the help of phenolic OH groups. Metals with variable valence are often involved in the generation of free radicals through the decomposition of hydrogen peroxide and lipid hydroperoxides, with the formation of hydroxyl or alkyl radicals, respectively. Flavonoids, by chelating the metal, can isolate these ions, and thus prevent the generation of free radicals. In addition, flavonoids and phenylpropanoids are oxidized by peroxidase, and hydrogen peroxide is utilized through the PC/AA/peroxidase system [10]. Total phenolic content (TPC) in plant products is strongly correlated with their antioxidant activity.

Studies of the last decade prove that simple carbohydrates in plant cells also perform the functions of antioxidants and signaling molecules [11]. Thus, on the one hand, an increase in the content of sugars (SAC) can be the cause of changes in the ROS generation by mitochondria, on the other hand, the activation of the pentose phosphate oxidation pathway can be a source of antioxidants. As a new concept, a theory is proposed, according to which soluble carbohydrates can participate in vacuolar antioxidant processes under stress [12]. According to this point of view, sugars that accumulate in significant amounts in vacuoles can act as scavengers of ROS, acting together with vacuolar phenolic compounds. It is believed that any saccharide in close proximity to any cell membrane has the potential to act as a ROS acceptor and contribute to membrane stability under stress conditions. During the storage of fruit and vegetable products, simple saccharides are formed during the degradation of polysaccharide components and at the same time are used to maintain the postharvest metabolism, which is the reason for the change in the concentration of soluble saccharides during the storage of vegetable products.

Three enzymes are mainly responsible for the enzymatic system of protecting the body against oxidative damage: superoxide dismutase, catalase, and peroxidase [8].

Superoxide dismutase (SOD) is one of the most important components of the system of protecting cells and tissues from oxidative destruction. Superoxide dismutase plays a central role in protection against oxidative stress in all aerobic organisms. SOD exists in four isoforms (CuZn-SOD, Mn-SOD, Fe-SOD, Ni-SOD) [7]. SOD is present in plant cells where redox processes involving oxygen occur. A comparison of data on the localization of different forms of SOD shows that CuZn-SOD is most abundant in plant cells. All isoforms of SOD are united by a single function – dismutation of superoxide radicals. Superoxide radicals are a source of formation of other ROS, including more reactive ones. Because hydroxyl radicals, singlet oxygen, and peroxynitrite actively oxidize protein molecules, there are no specific deactivator enzymes for these reactive oxygen species (ROS). Instead, their levels in the cell are indirectly regulated by SOD through the utilization of superoxide radicals, which are the source of their formation. Hence, SOD serves as the primary line of defense against oxidative damage by interrupting the oxidation of cellular macromolecules at the initiation stage.

The result of dismutation of superoxide anions is hydrogen peroxide, therefore, utilizing hydrogen peroxide is a necessary link in plant antioxidant protection. In the cell like this, it is provided by such enzymes as catalase and peroxidase – part of the second line of defense against ROS. Catalase (CAT) catalyzes the conversion of H_2O_2 into water and O_2. It is believed that catalase does not have a high affinity for H_2O_2 and cannot efficiently neutralize this compound at the low concentrations present

in the cytosol. In peroxisomes, where the concentration of hydrogen peroxide is high, catalase actively destroys it. However, catalase is practically absent in some cell compartments, so there is a need for the functioning of other enzymes involved in the detoxification of hydrogen peroxide.

Peroxidases (PODs) catalyze hydrogen peroxide reduction reactions involving various substrates. In dependence of the substrate, peroxidases are divided into three groups. Guaiacol peroxidase is present in cell walls and vacuoles, where it reduces hydrogen peroxide due to the oxidation of phenolic compounds. Ascorbate peroxidase is involved in the H_2O_2 detoxification in the cell due to the oxidation of ascorbic acid. In addition, glutathione peroxidase is present in plant tissues. This enzyme can potentially use glutathione to reduce hydrogen peroxide. In general, peroxidases, reacting with hydrogen peroxide, form substrate oxidation products and water. Some scientists single out the vacuolar ascorbate/phenol/peroxidase system as an important component of the antioxidant complex [13].

Endogenous antioxidants contained in vegetables create an inner circle of antiradical protection, which contributes to the preservation of their natural quality and nutritional properties. As a result of the disruption in the synthesis pathways of substances essential for normal metabolism, the system of antioxidant control over the generation of reactive oxygen species (ROS) functions properly only for a limited duration. When irreversible aging processes develop, the ROS level increases dramatically [14] and the antioxidant defense capabilities exhaust, which leads to a number of metabolic disorders and cell death.

A well-functioning antioxidant system is necessary to protect against postharvest stresses, maintain the quality of vegetables during storage, and prevent postharvest physiological disorders. A reliable relationship between the endogenous pool of antioxidants and the preservation of fruit and vegetable products has not been established. However, the formation of a powerful system of antioxidant protection can contribute to increasing the preservation of vegetables.

1.4 Regulation of postharvest metabolism by exogenous substances

Application of coatings on the surface of fruit and vegetable products has been actively used since the beginning of the 2000s. In contrast to synthetic polymer packaging, biodegradable coatings offer a more environmentally friendly solution. The use of edible coatings can be an effective strategy for maintaining the endogenous system of vegetables and ensuring their quality during a long period of storage. Such coatings can also affect the shelf life, reducing losses and helping to preserve

the valuable properties of vegetables. Edible coatings act as an additional layer that covers the stomates. The main function of edible coatings is to limit respiratory gas exchange and transpiration, hence slowing down the ripening and aging process of the fruit. Such coatings can be used as an alternative method of protection against oxidative stress and food spoilage. However, the gas permeability of the coating could prevent the development of anaerobic fermentation and undesirable changes in taste qualities. From a practical point of view, achieving such an effect can be noticeably difficult.

Edible coatings can be produced from various biopolymers. Among the most widely used are various natural polysaccharides (chitosans, alginates, pectins, starches, cellulose derivatives, carrageenans and gums), protein polymers (caseinates, milk protein concentrate, whey protein, gelatins, zein, gluten) and lipid components (waxes, paraffin, essential oils, resins, actoglycerides, emulsifiers and plasticizers) [15].

Ideal coatings should meet many requirements, namely:

– be generally recognized as safe;

– do not grant vegetables an extraneous smell and taste;

– be transparent and not affect the natural color of the fruit;

– ensure the slowing down of breathing and evaporation of moisture;

– maintain a normal level of oxygen in the tissues, preventing the creation of anaerobic conditions;

– possess antimicrobial properties;

– have a melting point above 40 °C;

– have low viscosity and high plasticity;

– dry well without additional measures;

– be non-sticky and non-brittle after drying.

Nowadays, however, edible coatings still have certain disadvantages. For example, natural polysaccharides, as a rule, are hydrophilic compounds, have low water resistance and unsatisfactory mechanical properties. At the same time, chitosan coatings have a good antimicrobial effect. Protein coatings significantly affect moisture and gas exchange, slowing down metabolism, but do not have bactericidal properties and can cause allergic reactions. Lipid coatings have hydrophobic properties, so they are an excellent barrier to moisture loss. Still, these coatings have unsatisfactory mechanical characteristics and are highly brittle. The mechanical properties of coatings are improved with the help of low-molecular plasticizers (glycerin, sorbitol, polyethylene glycol). On the other hand, such compounds change the organoleptic properties of products, so their use is undesirable.

Several recent scientific studies consider the possibility of obtaining edible and biodegradable films by combining different polysaccharides, proteins and lipids.

Their goal is to leverage the properties of each component effectively and attain synergy among them. The mechanical and barrier characteristics of these coatings depend not only on the compounds used in the polymer matrix, but also on their interaction and compatibility. Improving the composition of edible coatings is recognized as one of the key problems of scientific research in this area. This task requires careful formulation of the components of the films so that they correspond to the properties of the specific fruits and vegetables to which their application is planned.

A new trend in edible coatings is the introduction of components with high biological activity to obtain desired properties and expand their functionality. Most often this applies to antimicrobial and antioxidant substances. After all, the constant increase in the amount of ROS due to the aging processes must be balanced by a pool of antioxidants. This concept, therefore, is utilized by introducing exogenous antioxidants into the composition of edible coatings. Using synthetic antioxidants for this purpose is currently limited because of their potential toxic effects. Moreover, consumers perceive use of the natural antioxidants as an advantage, although they possess weaker antioxidant activity. The addition of such antioxidants as ascorbic acid, citric acid, resveratrol or tocopherol to the composition of edible coatings was demonstrated [16]. Essential oils and natural phenolic compounds are also often used. Extensive research on natural antioxidants for preserving fruit and vegetable raw materials is driven by their additional properties. In particular, flavonoids were shown to cause anti-carcinogenic, antibacterial, anti-allergic and antiviral effect.

The efficiency of storage significantly varies depending on the concentration of processing substances, storage conditions, and the type of fruit along with its characteristics. The effect of exogenous antioxidants is also dose-dependent. For example, in case of agave storage, a combined coating based on sodium caseinate and gum arabic with cinnamon and lemongrass oils in different concentrations was used. The use of cinnamon oil and lemongrass oil at a concentration of 1 % made it possible to obtain good color characteristics of guava (L^* value varied between 63–72). However, when both oils were used at a concentration of 2 %, the color characteristics were significantly degraded (L^* value was 39). In addition, at higher concentrations of essential oils, the content of ascorbic acid and the overall antioxidant activity of guava decreased [17], which is evidence of a pro-oxidant effect.

Maintaining the pro-antioxidant balance in plant tissues is crucial for preserving the quality of vegetables in the postharvest period. High doses of certain antioxidant compounds can be toxic, due to their pro-oxidant effects or the ability to react with physiological concentrations of ROS, which are necessary for the optimal functioning of the cell [18]. Such an extreme dependency of antioxidant effectiveness on concentration poses a significant obstacle to their widespread utilization. Namely, when

using antioxidants in edible coatings for a different type or variety of vegetables, it is necessary to check the effectiveness of the selected concentrations each time experimentally. As a consequence, when conducting research, the selection of effective concentrations of exogenous antioxidants takes a lot of time and labor resources.

To bolster the potency of the endogenous antioxidant system, it's logical to set concentrations of exogenous biologically active substances based on the evaluation of the plant organism's antioxidant status. In other words, concentrations of exogenous antioxidants should be inversely correlated with the endogenous pool of antioxidants.

1.5 Integral assessment of the antioxidant status of vegetables

Antioxidant status can be defined as the overall ability of a system or organism to neutralize free radicals and prevent oxidative stress. In contrast, "antioxidant activity" is a specific indicator or measure of the ability of a particular antioxidant or group of antioxidants to neutralize free radicals. Antioxidant activity is measured in percentages or other units of measurement and indicates how effectively a particular antioxidant is able to prevent oxidation.

The integral assessment of the antioxidant status of the system is a challenging task. Laboratory methods for assessing total antioxidant activity have a number of features that limit the possibilities of their application. Neither method measures all the antioxidants present in the system. The tests are limited to estimation of the effect of oxidatively active antioxidants, and therefore do not measure the catalytic effect of high molecular weight antioxidants. Some methods can be less specific and determine content of not only antioxidants, but also other compounds. Number of biologically active substances in plants do not necessarily have a pronounced antioxidant effect, but can still cause interference during analysis, leading to inaccurate results. Some processes in sample preparation (grinding, stabilization) before analysis itself might alter antioxidant properties of the sample, which makes the results less accurate. Today, there is no universally accepted "standard" method for determining antioxidant status, and even with the same method, reaction conditions can vary greatly in different laboratories, thus creating difficulties for interpretation and operation with results obtained by other researchers. Some variability in results, available in the literature, may arise from differences in the chosen measurement methods or from individual differences between samples. It is worth noting that laboratory methods of research require specialized equipment and are labor intensive, which makes them less reasonable to use on a mass scale or in settings where rapid assessment is required.

The obtained information is not always direct, which additionally complicates interpretation of results and determination of the exact relationships.

In such cases, it is advantageous to ensure the accuracy of judgments using mathematical methods. While there are numerous methods for tackling complex multi-criteria problems, most of them come with significant limitations and shortcomings that restrict their applicability. Previously [19] we suggested to use the Analytic Hierarchy Process (AHP), developed by T. Saaty [20] for the mathematical assessment of the antioxidant status of fruits and vegetables. Hierarchy analysis method is widely used in project management, decision-making, strategic planning and other areas. It allows to systematize and coordinate various aspects of decision-making and determine their importance in a hierarchical structure.

The primary drawback of AHP is arguably the subjectivity of evaluation judgments. However, an undeniable advantage of AHP is its capability to accommodate the variation in measurement units of the components within the antioxidant system. This method enables the comparison and assessment of the antioxidant status of any type of product. The subjectivity of the assessment can be mitigated by relying on experimental or analytical data regarding the quantitative indicators of the chemical composition.

The basic idea behind AHP is to break down a complex solution into smaller, more manageable steps. The process includes the following stages:

1. Hierarchy creation: breaking down the problem on the levels of criteria and alternatives to form a hierarchical structure.

2. Pairwise comparison analysis: evaluating the importance of each element of the hierarchy by means of pairwise comparisons. A matrix of pairwise comparisons is usually used to obtain numerical values of importance.

3. Element importance calculation: calculating the importance of each element using mathematical operations such as generalized eigenvalues.

4. Decision synthesis: making decisions and comparing alternatives based on the calculated importance.

5. Sensitivity to changes: providing assessment of the impact of changes in the input data or decisions made on the final result.

The step of creating hierarchies in AHP is considered as the initial step in solving a complex problem or making decisions. This stage includes defining the goal and creating a hierarchical structure by breaking down the problem into component parts. For example, here the AOS evaluation of asparagus of three different color varieties (green Prius, green-purple Rosalie and purple Erasmus) is demonstrated. Experimental data of the asparagus biochemical composition were obtained by our group under the identical laboratory conditions and averaged (**Table 1.1**).

Table 1.1 The content of antioxidants in asparagus

Antioxidants	Prius	Rosalie	Erasmus
AA, mg·100 g^{-1}FW	18.04	22.68	13.64
TPC, mg·100 g^{-1}FW	93.90	94.15	98.82
CAR, mg·100 g^{-1}FW	3.76	4.39	4.12
SAC, g·100 g^{-1}FW	2.63	2.89	2.95
SOD, % inhibition of adrenaline auto-oxidation	108.55	101.26	119.32
CAT, μmol H_2O_2·g^{-1}·min^{-1}	43.27	59.83	62.13
POD, μmol H_2O_2·g^{-1}·min^{-1}	59.94	24.62	68.97

The built structure includes three levels: a global criterion (general goal – integral assessment of AOS), a level of criteria (individual antioxidants of the system) and a level of alternatives (species or varieties of vegetables) (**Fig. 1.1**).

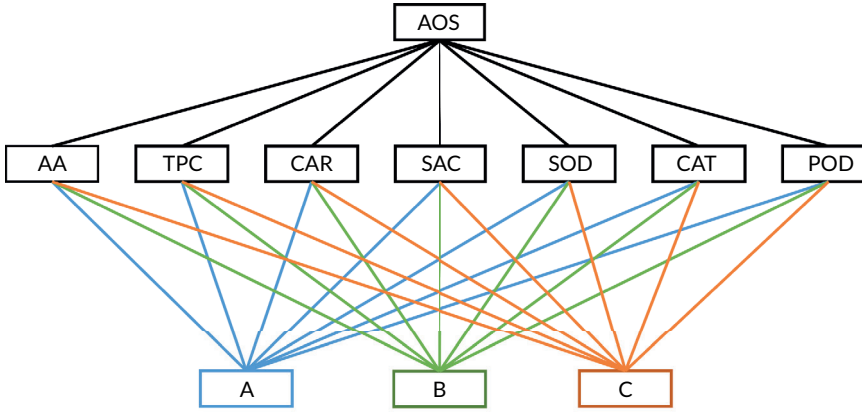

Fig. 1.1 Hierarchical structure of antioxidant status assessment of three vegetable varieties

Depending on the available experimental or analytical data on the components of the antioxidant protection system of a specific species or variety of vegetables, the criteria of the hierarchy can be supplemented with other antioxidants or changed, as well as sub-criteria can be evaluated. For example, it is possible to base evaluation not on the total content of phenolic substances, but on content of phenolic acids or flavonoids, or to consider them as sub-criteria of the hierarchy.

At each level of the hierarchy, the importance of elements relative to each other is determined. Experts rank each criterion and alternative relative to the global criterion. For this, the procedure of pairwise comparisons is used, where for each pair of elements their relative influence or importance is evaluated. When assessing the importance of each antioxidant, it's essential to consider their individual contributions to the antioxidant system (AOS), as well as correlations between components and with markers of oxidative stress like malondialdehyde. This approach helps mitigate subjectivity in the assessment process. This approach allows to systematize and take into account various aspects of antioxidant activity ensuring objectivity in decision-making.

For each level, a matrix of pairwise comparisons is created, where elements relative to each other receive numerical values, reflecting the degree of their importance. To present the results of assessments in quantitative terms, T. Saaty introduces a pairwise comparison scale [20] (**Table 1.2**).

Table 1.2 The pairwise comparison scale by T. Saaty

Relative importance (score)	Definition	Explanation
1	equal importance	both elements contribute equally
3	one element is slightly more important than another	experience and judgement slightly favour one element over another
5	strong advantage	experience and judgement strongly favour one over the other
7	very strong advantage	the dominance if one element is efficiently demonstrated in practice
9	absolute superiority of one over the other	the evidence favouring one element over another is of the highest possible order of affirmation
2, 4, 6, 8	intermediate scores between adjacent statements	a compromise decision
Reciprocal values of the above-mentioned scores	if one element is assigned a number between 1 and 9 when comparing it with another, then when comparing the second element with the first, the reciprocal value is obtained	a reasonable assumption

According to this scale, the difference in units of measurement does not matter. The scale involves a pairwise comparison of the weight (importance) of each element

with the weight of other elements of the set, which is carried out using expert judgments that are quantified. The primary advantage of the method is its dimensionless nature, eliminating issues when converting to the same units of measurement (**Table 1.3**).

Table 1.3 Pairwise comparison matrix for the set of criteria

Antioxidant	AA	TPC	CAR	SAC	SOD	CAT	POD	Eigenvector	Priority vector
AA	1	3	3	5	1	1	1	1.7226	0.1833
TPC	1/3	1	2	4	1/5	1/5	1/4	0.5959	0.0634
CAR	1/3	1/2	1	4	1/5	1/5	1/4	0.4888	0.0520
SAC	1/5	1/4	1/4	1	1/7	1/7	1/5	0.2437	0.0259
SOD	1	5	5	7	1	3	4	2.9827	0.3174
CAT	1	5	5	7	1/3	1	2	1.9737	0.2100
POD	1	4	4	5	1/4	1/2	1	1.3895	0.1480
Σ								9.3967	1.0000
λ_{max}									7.4982
C.I.									0.0830
C.R.									0.0629

To obtain priority estimation from the matrix, an algorithm is employed, which follows a schematic form like the following:

1. According to the approximate formula, the main eigenvector of the matrix is determined as the geometric mean of the corresponding row:

$$w_i = \sqrt[n]{\prod_{j=1}^{n} a_{ij}}, \tag{1.1}$$

where w_i – components of the eigenvector; n – matrix dimension (7 in the current example); a_{ij} – components of the matrix, $i \in \{1...n\}$, $j \in \{1...n\}$.

Hence: $w_1 = \sqrt[7]{1 \cdot 3 \cdot 3 \cdot 5 \cdot 1 \cdot 1 \cdot 1} = \sqrt[7]{45} = 1.7226$, etc. (**Table 1.2**).

2. The found components of the eigenvector are normalized:

$$v_i = \frac{w_i}{\sum_{i=1}^{n} w_i}, \tag{1.2}$$

where v_i – components of the normalized vector.

$\sum_{i=1}^{7} w_i = 9.3967$, thus:

$v_1 = \frac{1.7226}{9.3967} = 0.1833; v_2 = \frac{0.5959}{9.3967} = 0.0634$; etc. (**Table 1.2**).

The consistency of the inversely symmetric source matrix of pairwise comparisons is equivalent to the condition of equality between its maximum eigenvalue λ_{max} and the number of compared objects *n*, i.e. $\lambda_{max} = n$. Therefore, as a measure of inconsistency, it is customary to consider the normalized deviation from *n*, called the consistency index. Consistency of priorities is calculated as a matrix consistency index:

$$C.I. = \frac{\lambda_{max} - n}{n-1}, \quad (1.3)$$

where *C.I.* – consistency index; λ_{max} – the largest eigenvalue of the matrix, which is found according to the standard algorithm available in online calculators.

The λ_{max} of the matrix of pairwise comparisons for the criteria level was calculated as 7.50. Then:

$$C.I. = \frac{7.5-7}{7-1} = 0.083.$$

To assess the degree of consistency of judgments, the index of consistency *C.I.* is compared with a random index. A random index is a consistency index calculated for a square *n*-dimensional positive inversely symmetric matrix, the elements of which are generated by a random number sensor for the range of values from 1 to 9 (**Table 1.4**).

Table 1.4 Random consistency index (*R.I.*)

Matrix size	1	2	3	4	5	6	7	8	9	10
R.I.	0	0	0.58	0.9	1.12	1.24	1.32	1.41	1.45	1.49

Having the consistency index and choosing from the **Table 1.3** random index for the given order of the matrix, the consistency ratio can be calculated:

$$C.R. = \frac{C.I.}{R.I.}, \quad (1.4)$$

where *C.R.* – consistency ratio; *R.I.* – random consistency index.

$$C.R. = \frac{0.083}{1.32} = 0.063.$$

The acceptable value of *C.R.* must be about 10 % or less. If *C.R.* exceeds these limits, the judgment in the matrix have to be checked. In our case, *C.R.* = 0.063, i.e. the received priorities are completely consistent. The ranking of AOs according to the calculated priority estimations is presented in the **Fig. 1.2**.

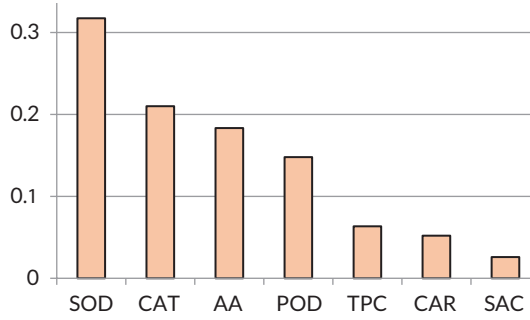

Fig. 1.2 Ranking of endogenous AOs in vegetable tissues

Based on **Fig. 1.2**, it's evident that SOD makes the maximum contribution to AOS, while sugars play a minimal role.

The next step involves comparing asparagus varieties based on second-level criteria. For each criterion, we compare the asparagus varieties by compiling 3×3 judgment matrices. According to the algorithm described earlier (formulas (1.1)–(1.4)), priority ratings and consistency of the matrix are calculated for each criterion. The matrix of pairwise comparisons for AA is characterized by an acceptable consistency of about 9 % (**Table 1.5**).

Table 1.5 Comparison matrix for AA

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	1/4	6	1.1447	0.2430
Rosalie	4	1	9	3.3019	0.7008
Erasmus	1/6	1/9	1	0.2646	0.0562
Σ				4.7112	1.0000
λ_{max}					3.1080
C.I.					0.0540
C.R.					0.0931

Rosalie has the highest priority for AA, and Erasmus has the lowest.

The matrix of pairwise comparisons for TPC allows to obtain an estimate of priority with a consistency of the matrix of about 1.5 % (**Table 1.6**).

Table 1.6 Comparison matrix for TPC

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	1/2	1/4	0.5000	0.1365
Rosalie	2	1	1/3	0.8736	0.2385
Erasmus	4	3	1	2.2894	0.6250
Σ				3.6630	1.0000
λ_{max}					3.0180
C.I.					0.0090
C.R.					0.0155

The maximum priority of PC is for Erasmus, and the minimum for Prius.

For carotenoids, the matrix consistency ratio is only 0.3 %. However, such a high degree of agreement can be a disadvantage and may indicate excessive confidence of experts in their judgments (**Table 1.7**).

Table 1.7 Comparison matrix for CAR

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	1/5	1/3	0.4055	0.1094
Rosalie	5	1	2	2.1544	0.5816
Erasmus	3	1/2	1	1.1447	0.3090
Σ				3.7046	1.0000
λ_{max}					3.0040
C.I.					0.0020
C.R.					0.0034

The consistency of the matrix for sugars is identical to the matrix for phenolic compounds (**Table 1.8**).

As can be seen from the **Table 1.8**, Erasmus asparagus has the highest priority in terms of sugar content.

According to SOD activity, the highest priority is typical for Erasmus. The constructed matrix has a consistency ratio of 4.7 % (**Table 1.9**).

Table 1.8 Comparison matrix for SAC

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	1/2	1/3	0.5503	0.1692
Rosalie	2	1	1	1.2599	0.3874
Erasmus	3	1	1	1.4422	0.4434
Σ				3.2525	1.0000
λ_{max}					3.0180
C.I.					0.0090
C.R.					0.0155

Table 1.9 Comparison matrix for SOD

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	3	1/4	0.9086	0.2176
Rosalie	1/3	1	1/6	0.3816	0.0914
Erasmus	4	6	1	2.8845	0.6910
Σ				4.1746	1.0000
λ_{max}					3.0540
C.I.					0.0270
C.R.					0.0465

The matrix of pairwise comparisons of asparagus by catalase activity allows to obtain estimations of priority with a consistency of about 2 % (**Table 1.10**).

Table 1.10 Comparison matrix for CAT

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	1/4	1/5	0.3684	0.0974
Rosalie	4	1	1/2	1.2599	0.3331
Erasmus	5	2	1	2.1544	0.5695
Σ				3.7828	1.0000
λ_{max}					3.0250
C.I.					0.0125
C.R.					0.0215

The largest catalase activity priority vector is typical for Erasmus, and the smallest for Prius. The matrix of paired comparisons of fruit and vegetables by peroxidase activity has a consistency ratio of 0.0560 (**Table 1.11**).

Table 1.11 Comparison matrix for POD

Asparagus	Prius	Rosalie	Erasmus	Eigenvector	Priority vector
Prius	1	5	1/3	1.1856	0.2789
Rosalie	1/5	1	1/7	0.3057	0.0719
Erasmus	3	7	1	2.7589	0.6491
Σ				4.2503	1.0000
λ_{max}					3.0650
C.I.					0.0325
C.R.					0.0560

Peroxidase activity has the highest priority for Erasmus and the lowest for Rosalie.

After determining the importance of all elements and constructing matrices of pairwise comparisons, an analysis is carried out to obtain the importance (weight) of each element. A synthesis of the hierarchy is carried out, which allows to consider all aspects and make the decision.

Global priorities, which will be integral assessments of the antioxidant status of asparagus varieties, are calculated using the following formula:

$$I_{AOS} = P_1^2 \cdot P_1^3 + P_2^2 \cdot P_2^3 + ... + P_n^2 \cdot P_n^3, \quad (1.5)$$

where I_{AOS} – integral assessment of antioxidant status; $P_1^2 ... P_n^2$ – priority evaluations of the matrix of criteria; $P_1^3 ... P_n^3$ – priority evaluations of the matrix of alternatives.

For asparagus of Prius variety:

$$I_{AOS} = 0.1833 \cdot 0.2430 + 0.0634 \cdot 0.1365 + 0.0520 \cdot 0.1094 +$$
$$+ 0.0259 \cdot 0.1692 + 0.3174 \cdot 0.2176 + 0.2100 \cdot 0.0974 + 0.1480 \cdot 0.2789 =$$
$$= 0.1940 \approx 0.19 \text{ (}\textbf{Tables 1.3, 1.5–1.11}\text{)}.$$

By similar calculations, we get:

– for Rosalie $I_{AOS} = 0.2934 \approx 0.29$;

– for Erasmus $I_{AOS} = 0.51245 \approx 0.51$.

The calculated integral evaluation shows that, among the studied varieties, the highest antioxidant status is in asparagus of the Erasmus variety, and the lowest

in asparagus of the Prius variety. Therefore, when applying exogenous edible coatings, the concentration of antioxidants in the composition can be adjusted according to the established antioxidant status. Such approach ensures the prevention of product losses during extended shelf life.

Conclusions

Reducing losses of fruit and vegetable products, particularly during storage, is a pressing issue that requires attention and technological advancement. Addressing these losses not only ensures a sustainable food resource but also aids in reducing greenhouse gas emissions and optimizing resource utilization.

Maintaining a well-functioning antioxidant system is crucial for preserving vegetable quality during storage and preventing postharvest disorders. Utilizing edible coatings with antioxidant properties emerges as an effective strategy for maintaining vegetable quality throughout the storage period. However, it is important to note that excessive antioxidant doses can potentially have toxic effects, and their efficacy is influenced by the concentration and type of vegetables.

To enhance the potency of the endogenous antioxidant system, it is vital to establish concentrations of exogenous antioxidants that correlate with the endogenous antioxidant pool in plant tissues. This approach ensures the maintenance of antioxidant status and quality preservation during the postharvest period. Here we propose a method that employs hierarchical analysis for objective assessment of vegetable antioxidant status.

While the hierarchical analysis method offers a systematic approach, it has drawbacks related to the subjectivity of the evaluation judgments. They can be omitted by integrating into calculations experimental or analytical data on chemical composition, as well as correlations between antioxidant system components and oxidative stress markers. The proposed integrated approach provides objectivity and aids decision-making in determining vegetable antioxidant status, thereby contributing to the prevention of product losses during extended storage.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 2

The advantages of using sublimation for preserving the antioxidant properties of cranberries

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Abstract

The benefits of using the sublimation method for preserving the antioxidant properties of cranberries have been studied. Cranberries are known for their antioxidant properties, which help combat infections, reduce the risk of heart disease, and improve arterial pressure. This berry is particularly beneficial in prostate cancer.

Most of the beneficial compounds in cranberries are found in their skin, which may lose its properties during traditional juice extraction. Drying is an alternative method for preserving antioxidants, but traditional methods can lead to a loss of product quality.

Sublimation drying has proven to be the most efficient and innovative method, as it ensures the preservation of cranberry antioxidant properties. After the sublimation cycle, the final moisture content of the material is only 2–5 % of the initial content, guaranteeing the maximum retention of beneficial properties and the production of a high-quality product. This method is promising for maintaining the quality of raw materials during drying and preserving their medicinal properties.

Keywords

Cranberry, drying technology, sublimation, nutritional value, antioxidant properties, phenolic compounds, polyphenolic compounds, anthocyanins.

2.1 The relevance of sublimation drying

In recent times, both in Ukraine and worldwide, the popularity of healthy eating is expanding, which includes consuming fresh or, for example, dried products such as berries and fruits. Providing the population with diverse high-quality and beneficial food products becomes an important task for the food industry. The benefits

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of products created by nature form the basis for healthy eating. Consumption of vitamins, micronutrients, and enzymes allows improving the quality of human life.

The drying process is widely used in the food industry to preserve the properties of berries. The use of modern methods contributes to the improvement of drying technologies. Products subjected to drying retain vitamins, nutrients, flavor qualities, color, and aroma, and can easily be reconstituted in various conditions [1].

For effective preservation of the properties of berries during drying, it is necessary to carefully justify the process and drying regime, as it involves complex thermophysical and technological processes. Currently, sublimation drying is considered the most efficient and innovative method for preparing berries and other products for preservation and long-term storage.

The first use of sublimation drying occurred in Paris in 1906 when electrophysiologist Jacques-Arsène d'Arsonval, along with his assistant Frédéric Bordas, first applied this process to preserve the rabies virus. This discovery contributed to the further development of the first vaccine in history against this disease.

Modern equipment for sublimation drying was developed during World War II, when a large number of wounded soldiers were successfully treated thanks to this technology. Additionally, serum was transported from the USA to Europe using a sublimator: previously, it was unsuitable for use in hospitals as a transfusion material because it spoiled during transportation. Initially, sublimation (lyophilization) drying was developed for commercial use to chemically stabilize serum without refrigeration. Subsequently, sublimation began to be used for storing antibiotics of the penicillin series, and this method also made it possible to preserve biological substances [2].

Today, the technological process of drying using sublimation is widely used in processing industries and for treating a wide range of substances. This methodology has become an integral component in industries such as pharmaceuticals, food processing, laboratory activities, and others. Sublimators (lyophilization equipment) are even used for restoring water-damaged documentation, carbohydrate research, and more.

The demand for processing food raw materials with a lyophilizer is due to the ability to evaporate ice without it transitioning into a liquid state. To perform ice sublimation, specific conditions need to be created. The advantage of preserving fruit and berry raw materials through sublimation drying, compared to other methods, is the possibility of further long-term storage of the product at room temperature. The advantage of the method lies in the significant evaporation of moisture during such sublimation processing, resulting in a natural reduction in the weight of the final product. This simplifies the further transportation and handling of the food products. The storage period consequently becomes longer, facilitating the distribution of high-quality products with high nutritional value.

High-quality freezing and sublimation drying today are made possible thanks to PIGO technologies [3]. In the "Yagidnyk" journal, the advantages of freezing and sublimation were discussed as a method for creating the maximum possible added value for products. While freezing allows for the complete preservation of all the nutritional values of food products, the subsequent stage – sublimation – enables the avoidance of all requirements regarding the cold chain and specific temperature conditions during prolonged storage and transportation, as well as modern preservation of the quality of fresh or frozen products. However, the quality of frozen and sublimated fruit and berry products depends on the equipment used by manufacturers. Today, the PIGO company is one of the few companies in the world that offers all three technologies for preserving food raw materials: freezing, drying, and sublimation drying. They refine existing technologies and introduce new solutions to achieve a higher quality end product.

Therefore, today, more and more producers and processors of berry products are paying attention to the method of storage and processing known as sublimation, which has recently been close to revolutionizing the food industry. This innovative, modern technology allows retaining up to 97 % of nutrients, vitamins, and micronutrients in the raw materials. Sublimated berries, fruits, and vegetables preserve their natural aroma, taste, color, and even their original shape, visually indistinguishable from fresh raw materials.

Such products preserve excellently without any preservatives for at least five years (without access to oxygen and water) while enduring temperature fluctuations (from −50 °C to +50 °C), which is a significant advantage compared to other preservation methods. The technological drying process is based on removing moisture from fruit and berry raw materials using heat or cold and heat until they reach a residual moisture level suitable for long-term storage [4].

The complexity of the components of fruit and berry raw materials in their chemical composition leads to quite profound physico-chemical, structural, and biochemical changes during moisture removal at elevated temperatures. This typically results in changes in organoleptic properties and the nutritional value of the product. The nature and extent of these changes depend on the composition and initial properties of the raw material, the methods and drying regimes employed, as well as the amount of moisture removed from the product.

The removal of moisture from the raw material during drying depends on the total moisture content and the type of moisture association with the material. Moisture association with the material is characterized by the amount of free energy of isothermal dehydration, i.e., the force required to remove 1 mole of water at a constant temperature without changing the chemical composition of the raw material.

If there is free moisture in the raw material, then the moisture energy will be zero. With the removal of moisture, the strength of its connection with the berry will increase, and the binding energy will increase. Thus, the lower the moisture content in the berry, the higher the value of the binding energy. If the raw material contains moisture that is subjected to temperature treatment or periodic exposure to moisture and heat, it will change its physical characteristics, affecting the bonds of absorbed liquid [5].

Fruit and berry raw materials are characterized by high moisture content, resulting in a significant amount of water (75–95 %), which creates a favorable environment for the growth of microflora causing spoilage, as well as for various enzymatic reactions and life processes. Therefore, various methods are used to remove moisture from fruit and vegetable products.

Each drying method has its own advantages and disadvantages, and fruit and vegetable products differ in their organoleptic characteristics. For example, products dried by sublimation retain their appearance, volume, color, and taste, and quickly regain their original properties. In turn, fruit and berry raw materials dried with infrared radiation appear better than those dried by convective methods. For solar drying, the raw material is spread out on trays and racks, exposed to direct sunlight in open spaces, or placed in the shade under a shelter with sufficient air circulation. While this drying method does not require significant expenses, it is rather time-consuming (4–20 days), and there is a risk of contamination of the fruit and berry raw materials with sand, dust, and infestation by flies, wasps, etc.

Thanks to modern developments in the technological process of sublimation drying, high-quality flat heaters are used for heating, capable of uniformly heating the product and compensating for heat losses during ice evaporation. Therefore, such equipment configuration for sublimation drying is currently in high demand among professionals [6].

Sublimation drying has also recently been used for the production of spices from various herbs: parsley, dill, basil, marjoram, rosemary, oregano, and other plants for seasoning dishes. Additionally, soluble coffee, various types of tea, and spices are also processed.

In today's world, where diets and weight control have become commonplace, the range of dried products is expanding, for example, through the production of berry snacks. As the number of competitors in the snack market increases, there is an opportunity to expand the range of "healthy" snacks. Consumers focused on a healthy lifestyle carefully scrutinize the product ingredients. They want snacks free from preservatives, flavor enhancers, and harmful additives. Approximately 60 % of consumers are willing to pay extra if it guarantees the quality of the product. Snacks containing

vitamins and micronutrients are popular. This has led to the development of the market for berry pastilles and fruit bars, which are distinguished by an increased amount of beneficial substances.

The technological process of sublimation drying is also known as lyophilization or sublimation. This process is widely used not only in the food industry but also in pharmaceuticals for drying vaccines and food supplements [7].

The technological process of lyophilization consists of the following stages, which must be carried out sequentially: pre-processing of the product – freezing – drying – packaging of the product.

The methodology of such drying, as well as the terms and method of storing food products, depend on their final chemical composition. For example, products containing animal protein should not be subjected to overheating after drying, as it may lead to protein denaturation. Fruit and berry products processed by the sublimation method should be isolated from contact with the surrounding environment, meaning they should be hermetically sealed; otherwise, the fats and vitamin components of the raw material may begin to oxidize. The degree of drying is determined by considering the portion of reducing substances, calculating the exact amount of moisture to be removed. Also, during the preparation of food raw materials for sublimation, a certain bacterial threshold of the products is ensured.

Freezing fruit and berry raw materials can be done either in a specially designed chamber or directly in the lyophilizer by creating a vacuum environment and partial evaporation of moisture. This method is much easier to perform compared to conventional freezing, but it may not be suitable for all food products. During vacuum freezing, the initial indicators of the biochemical composition of the raw materials are lost, so raw meat, fish, as well as juices and purees, are not recommended to be frozen using the vacuum method.

Lyophilization has its technological peculiarities, namely: during pre-freezing, thawing of the raw material before drying must be avoided. During sublimation, products lose between 70 to 90 % of their moisture, and final drying is carried out at positive temperatures. At each stage of drying, the temperature threshold is regulated by technological parameters. The main requirement for maintaining a specific temperature of the product is its biochemical properties and the drying cycle. Different types of raw materials require specific temperature parameters for the sublimation process. More often, the temperature ranges from −15 to +35 °C, but juices from fruit and berry raw materials require temperatures within the range of −25 °C due to their high carbohydrate content, while animal-origin raw materials require temperatures of −16 to −20 °C. During the sublimation stage, approximately 50 % of the moisture evaporates, and about 60 % of the processing cycle time is spent.

At the next stage, the drying of food raw materials is carried out at high temperatures, where the final removal of moisture from the product occurs. To maintain the biochemical composition at a high level and ensure product quality, temperature parameters must precisely meet technological requirements. The duration of processing is significant and depends on the technological process. During the drying stage, the temperature range is between +45 to +85 °C, and the duration can be up to 40 % of the total processing cycle, resulting in a loss of up to 30 % moisture.

One advantage of lyophilization is the preservation of the beneficial properties and taste of the product. The structure of the product becomes porous, which promotes sorption processes: at the beginning of storage, the products actively absorb oxygen, leading to rapid oxidation, and also adsorb moisture, significantly reducing the quality of the raw material. Therefore, to prevent adsorption, it is recommended to compress processed products before packaging, eliminating contact with the surrounding environment. The dried raw material cannot be stored without airtight packaging, so packaging is done immediately after drying. Polymer packaging is most commonly used, incorporating aluminum foil as a component of the packaging. Polymer films also have excellent operational properties, low weight, and high strength.

2.2 The chemical composition and biological value of cranberries

Cranberry is a sour berry that is considered one of the healthiest berries due to its unique content of mineral salts and bioactive substances. It is typically added to juices, sauces, and food supplements. Additionally, dried cranberries are an excellent alternative to raisins for baking or garnishing various dishes.

The chemical composition of cranberries includes vitamins: B1, B2, B6, B9, B12, K, C, A, E, PP; minerals: potassium, sodium, calcium, magnesium, phosphorus, iron, iodine, silver, copper, lead, barium, manganese. In addition, flavonoids, glycoside vaccinine, triterpene acids – oleanolic and ursolic, organic acids – benzoic, citric, quinic, and oxoglutaric have been found in them. Cranberries also contain sugars such as glucose, fructose; polyphenols: quercetin, myricetin; pectin, tannins, nitrogenous and coloring substances, and phytoncides, cyanides. In particular, about 30 types of organic acids have been found in the berry, and the large amount of benzoic acid allows cranberries to be stored throughout the winter without thermal processing and the addition of preservatives. The chemical composition of fresh cranberries (according to the Nutrition resource) [8] is presented in **Table 2.1**.

In summary, fresh cranberries are nutrient-dense fruits rich in vitamins, minerals, and dietary fiber, making them a valuable addition to a balanced diet.

Table 2.1 Chemical composition of fresh cranberries

Titles	Content per 100 g of raw material	Daily intake requirement
Vitamin C	13.3 mg	22 %
Vitamin E (tocopherol)	1.2 mg	6 %
Vitamin K (phylloquinone)	5.1 mcg	6 %
Vitamin B1 (thiamine)	0.02 mg	10 %
Vitamin B2 (riboflavin)	0.02 mg	10 %
Vitamin B3 (pantothenic acid)	0.30 mg	2.5 %
Vitamin B6 (pyridoxine)	0.1 mg	5 %
Vitamin B9 (folic acid)	1.0 mcg	0.5 %
Vitamin PP (niacin)	0.4 mg	2.5 %
Calcium	14.0 mg	1.4 %
Potassium	105.0 mg	2 %
Magnesium	15.0 mg	5 %
Phosphorus	11.0 mg	1 %
Copper	0.1 mg	3 %
Iron	0.6 mg	7.5 %
Manganese	0.4 mg	18 %
Carbohydrates	12.2 g	4 %
Proteins	0.5 g	0.4 %
Fiber	4.6 g	23 %

Cranberries are included in many dietary supplements, herbal remedies, sauces, and other food products due to their unique content of mineral salts and bioactive substances, making them one of the most beneficial berries.

Cranberries are also a source of antioxidants, specifically polyphenols, including quercetin, myricetin, peonidin, malvidin, and delphinidin. Along with cyanidin and peonidin, these compounds are responsible for the rich red color of cranberries.

Antioxidants are primarily found in the skin of the berry, so there are significantly fewer of them in cranberry juice. This berry has physiological effects on the human body, possessing antioxidant, refreshing, and toning properties. It improves physical and mental performance, stimulates the secretion of gastric and pancreatic juices, exhibits antimicrobial and diuretic effects. The potent antioxidants in the berries fight various infections (bacterial and viral) and lower the level of "bad" cholesterol, while plant compounds have a protective effect.

Cranberries also reduce the risk of heart disease, lower blood pressure, and inhibit the formation of a compound called homocysteine, which is known to damage the lining of blood vessels. Adding cranberries to one's diet can help manage several risk factors for cardiovascular diseases, including systolic blood pressure (the blood pressure level against the walls of the arteries during heart contractions). Cranberries contribute to reducing body mass index (BMI) and improving levels of "good" cholesterol.

Some dietitians classify cranberries as superfoods, which are predominantly plant-based products with high levels of beneficial nutrients. This berry contains powerful antioxidants that fight infections, lower "bad" cholesterol levels, and possess anti-inflammatory properties. Cranberries can be particularly beneficial in prostate cancer due to the presence of ursolic acid, which has antioxidant and anticancer effects. It is believed that this berry is particularly beneficial in prostate cancer due to the presence of ursolic acid, a plant compound with antioxidant, anti-inflammatory, and potential anticancer properties [9, 10].

Cranberries improve the taste of food, promote better digestion, and enhance food absorption. Some dietitians refer to cranberries as stimulators of pancreatic secretion, as they enhance the secretion of the pancreas. In cases of pyelonephritis, cranberries enhance the antibacterial action of other medications, thus contributing to their therapeutic effect.

In medicine, cranberries are recommended for patients recovering from severe illnesses. They have a toning and refreshing effect and enhance the mental and physical abilities of the human body.

The berry possesses bactericidal properties: cranberry juice inhibits the growth and development of *Staphylococcus aureus*, *Escherichia coli*, and *Salmonella bacteria*, reducing the risks of developing ulcerative diseases. Infection caused by the Helicobacter pylori bacterium is considered the main cause of stomach inflammation and ulcers. Therefore, the phenolic compounds of cranberries exhibit 9 % inhibition of urease activity, so consuming cranberries may inhibit Helicobacter pylori in the gastrointestinal tract.

However, this berry is not beneficial for everyone, as it is not recommended for patients with stomach ulcers. Its consumption in such conditions is only advisable under the recommendation of a doctor depending on the individual's condition [11].

Dried cranberries are recommended for the prevention and treatment of urinary tract infections. Such infections are caused by the bacterium *Escherichia coli*, which attaches to the inner surface of the bladder and urinary tract. Thanks to the presence of type-A proanthocyanidins, which possess anti-adhesive properties, cranberries can prevent the development of the disease.

Consuming dried cranberries strengthens the immune system, prevents the formation of kidney stones, cleanses the lymphatic system from cholesterol, removes heavy metals from the human body, treats and prevents gastritis and ulcers, and also prevents the rapid growth of tumors.

Dried cranberries are obtained by dehydration, which involves removing moisture from fresh cranberries (Vaccinium Oxycoccos) with the addition of sugar to neutralize acidity. Some manufacturers, in the production of dried cranberries, coat them with a small amount of vegetable oil to prevent them from sticking together. For example, in the United States, they are called "craisins", akin to our raisins. They contain such microelements as phosphorus and magnesium, manganese, potassium, iron, and zinc, as well as calcium and copper. The vitamin complex includes vitamins B6, B12, E, C (20 % of the daily norm), K, and A.

Flavonoids in dried cranberries reduce the amount of cholesterol that deposits on the walls of arteries, thereby protecting the body from atherosclerosis, while antioxidants repair cells in the cardiovascular system damaged by free radicals.

Dried cranberries are extremely beneficial for the health of the human digestive system. In folk medicine, they are featured in many recipes as an effective remedy for stomach and duodenal ulcers. They are also considered as a remedy for cancer due to their anti-tumor properties. "Dehydrated" northern berries are characterized by a high content of vitamin C and antioxidants, which are capable of inhibiting the development of malignant cells, for example, in breast cancer. Moreover, regular consumption of dried cranberries reduces the risk of osteoporosis and joint diseases.

Thanks to the unique chemical composition, dried cranberries prevent bacteria from sticking to tooth enamel, thus blocking the formation of dental plaque and preventing tooth decay. This also leads to improved oral health. According to the Center for Oral Biology proanthocyanidins benefit oral health by preventing bacteria from adhering to the surface of teeth.

2.3 Technological process of sublimation in the production of dried berries

Dehydration or sublimation drying is used to preserve the antioxidant properties of fruit and berry products, as well as any ingredients. Both methods allow preserving the freshness and nutritional value of the product for a long time. Thus, fruits, berries, and vegetables can be consumed not only during their typical ripening seasons but also throughout the entire year.

Technological lines enable the organization of continuous flow production of goods, including sequential preparation of raw materials and materials, technological

operations, and packaging of finished products. In the technological line, all production operations are performed in a specific sequence, taking into account the main technical and economic indicators.

The dehydrator, as one of the components of the technological line, is unique equipment designed for drying berries, fruits, vegetables, and so on. With the help of the dehydrator, moisture is removed from the raw materials, and then they are placed in a freezer to preserve them for a long period. The dehydration process is extremely simple and does not require any excessive effort; processing occurs automatically. The product, after thawing, retains its unique taste and aromatic properties almost unchanged, and any changes in appearance occur due to dehydration, which is the basis of the dehydrator's operation.

The dehydration and drying processes occur as follows: the food dehydrator removes water from the product by air circulation at low temperatures.

To ensure that plant raw materials remain preserved for as long as possible, it is necessary to remove moisture, as such products deteriorate very quickly. The processes of decay occur as a result of bacterial action, which initiates chemical processes in the structure of biomaterials. The main factors under which bacteria degrade the quality of raw materials are temperature – as bacteria become active only at certain temperatures, and moisture or water. Thus, by altering both factors, their shelf life can be extended. Dehydration removes a high percentage of moisture contained in the raw material, but to extend the shelf life of the product, it is necessary to subject it to drying, that is, to carry out the process of complete dehydration of the raw material.

Sublimation drying can occur under vacuum or at normal atmospheric pressure. The process at low temperature and atmospheric pressure takes a considerable amount of time, so equipment capable of creating a vacuum is used to expedite it. Decreasing the pressure enhances more efficient evaporation by increasing the mass transfer coefficient. Since vacuum drying takes place in a sealed chamber, convective heat transfer is insufficient. To ensure intensive evaporation in a vacuum environment, heat is generated to evaporate moisture, which is then transferred to the products through heat conduction from heated metal surfaces (via contact with electric heaters) or through radiation from heated screens (using infrared radiation) [1].

The sublimation process consists of three sequential stages: product preparation, freezing, sublimation, and the final drying stage.

Initially, the product is frozen to temperatures lower than its solidification point. This creates ice crystals in the berries, which disappear during the sublimation stage. During the sublimation stage, the main drying process occurs – slow, uniform heating to the temperature at which water transitions from a solid to a gaseous state.

The freezing stage affects the quality of the final product; if it is conducted very rapidly and deeply, the ice crystals will be small and will evaporate very quickly. Drying requires the application of heat at a temperature not exceeding 40 °C.

The principle of operation of a sublimation-vacuum dryer lies in the fact that at low atmospheric pressure (the "triple point" threshold, calculated for water at a pressure of 0.01 °C 611, 657 Pa), water exists only in solid and gaseous states. Therefore, under these conditions, vapor can directly convert to ice without passing through the liquid phase.

During the technological process of sublimation, it is important to adhere to the sequence of stages, which include:

1. Preparation of the substance or product for drying, which may involve concentrating the products, modifying their composition, reducing vapor pressure, or increasing the surface area of the product. Pieces of the product may be individually frozen to transfer the solvent to a free state before the drying stage.

2. Freezing, which can be done, for example, in laboratory conditions using a special rotating flask in a "shell freezer". This process increases the surface area of the product to accelerate drying. In industrial settings, freezing occurs in lyophilization equipment, where the material is cooled below its triple point to ensure optimal sublimation. The triple point refers to the freezing period when the liquid in the raw material can simultaneously exist in three phases: liquid, solid, and gaseous. This feature guarantees sublimation rather than melting, and the large crystals formed during freezing are better suited for sublimation. To obtain such crystals, either freezing must be carried out for a long time or the temperature must be cyclically raised and lowered. However, this type of freezing is not suitable for berry production because they freeze slowly, affecting their texture and reducing nutritional value. Therefore, fruit and berry raw materials need to be rapidly frozen to prevent crystal formation altogether. The freezing stage is one of the most critical phases of the entire sublimation process. If not properly executed, the raw material becomes unsuitable for further processing.

3. The primary stage of drying involves reducing pressure while delivering heat to the product to sublimate ice. During this phase, approximately 95 % of the liquid is removed from the product. It is not advisable to accelerate this process because excessive heat can severely disrupt the structure and damage the raw material. The pressure in the chamber can be controlled using a partially formed vacuum aimed at accelerating drying. The condenser cold chamber and condenser plates contribute to the secondary freezing of the liquid. The condenser does not affect the freezing of the product; instead, it prevents vapor from entering the vacuum pump and operates at a temperature of less than –50 °C.

4. The secondary drying stage involves the removal of unfrozen liquid molecules, while the remaining ice has already sublimated. Lyophilization is regulated here by the isotherms of material adsorption. The drying temperature environment is higher than in the first stage and may even be above 0 °C. The pressure is lowered to stimulate desorption.

After the sublimation process is complete, the vacuum environment created in the working chamber is replaced by inert gases, and the dried product is sealed. The final water content in the product after sublimation can be a maximum of 4 %.

Adhering to the conditions is the key to quality sublimation drying. Therefore, the majority of moisture in the product should be present in the frozen state, and the total volume of ice should not be less than 70 % of the product's weight. It is essential to control the sublimation of ice by monitoring the pressure difference between the vapor emissions above the product's surface and the vapor in the chamber. Maintaining the pressure level is crucial because precise indicators ensure the transition of ice into a vapor state bypassing the liquid phase. Condensation of vapor emissions should be carried out using special evaporative devices.

During the drying process, the berries reach a certain temperature and release heat during the evaporation of ice. To compensate for heat losses and maintain a specific temperature regime, continuous heat supply is necessary. The vapor generation boundary gradually shifts from the surface layers of the raw material to its center, complicating effective heat transfer. Therefore, sorted berries should be stored at room temperature before loading into the sublimator. After the equipment is turned on, the vacuum pump reduces the pressure in the chamber to 10–30 Pa.

Thanks to the vacuum environment and partial evaporation of moisture, the raw material begins to freeze. A larger percentage of the raw material's moisture transforms into crystalline ice. Then the technological process of sublimation occurs. Due to the operation of the vacuum pump, the moisture that has turned into vapor is transferred to the desublimator, and the air from it enters the atmosphere. The final stage of the sublimation drying process is the activation of heaters, which provide heat, thereby removing the remaining moisture from the product. The equipment also includes a defroster section for thawing the ice.

So, let's outline the main steps of sublimation:

Step 1. Preparation. Cleaning the berries, the possibility of disinfection, and then loading the tray with prepared berries into the drying chamber.

Step 2. Freezing. A vacuum is created in the chamber, and cranberries are cooled to their solidification temperature. The better the freezing (considering the speed and depth of freezing), the finer the ice crystals will come out in the berries, and the faster they will then turn into vapor.

Step 3. Sublimation. The frozen berries are slowly heated to the point where ice transitions into vapor, which is directly the process of drying the raw material. After removing the water, the dried berries should be placed in a sealed package for at least twenty hours.

The use of freeze-drying is a modern method of producing berry snacks. Plant-based and berry snacks, such as cranberry pastille, can be utilized in special diets for individuals following a vegetarian or healthy eating regimen, or those with dietary restrictions or allergies. Today, employing such a production method for cranberry pastille allows for significant expansion of the market for antioxidant-rich products and meets consumer demand.

2.4 Assessment of the nutritional value and antioxidant properties of cranberries

Berries naturally have capillaries and a porous structure. The membrane of the capillaries is elastic and swells during moisture absorption. During moisture removal, the berry undergoes shrinkage and may become brittle.

Fresh cranberries have a high-water content and a low percentage of dry matter. Most of the beneficial compounds in cranberries are found in the berry's skin and may be lost during juice extraction. Since it's impossible to eat fresh berries year-round, dried berries can serve as an alternative source of beneficial compounds and valuable antioxidants.

The assessment of the nutritional value and antioxidant properties of cranberries was conducted using standard methodologies [12].

The organoleptic evaluation of fresh and dried berries was conducted using expert tasting methods, with pre-prepared evaluation forms using a 5-point scoring system. The obtained results were averaged and presented in a radar chart. Calculations of the results and the significance of the research factors were performed using the statistical computer program Excel with the QIMacros® add-on.

Quantitative determination of anthocyanins and flavonoids content was carried out using spectrophotometric methods.

The energy value was determined using energy coefficients: 1 g of fats – 9.0 kcal (37.7 kJ); 1 g of carbohydrates – 3.75 kcal (15.7 kJ); 1 g of starch – 4.1 kcal (17.2 kJ); 1 g of organic acids – 2.5–3.6 kcal (10.5–15.1 kJ); 1 g of proteins – 4.0 kcal (16.7 kJ). The actual caloric content of the raw material was calculated taking into account the digestibility coefficients: proteins – 84.5 %, fats – 94 %, carbohydrates – 95.6 %.

To determine the energy value in the International System of Units (SI), i.e., in kilojoules, the conversion coefficient was used: 1 kcal = 4.186 kJ. The energy value of the product was calculated per 100 grams of edible portion.

To assess the quality of the raw material, a sensory evaluation of cranberries was conducted based on organoleptic indicators. In order to determine changes in quality indicators, experimental batches of dried (sublimated) berries of two varieties, "Black Veil" and "Washington", were prepared. The tasting was conducted for fresh and dried cranberries, and the results of the organoleptic evaluation of the product quality are presented in **Table 2.2**.

The cranberries subjected to sublimation drying were in a stage of technical ripeness, which was determined by their size, external appearance, color, characteristic taste and aroma, and consistency. Only high-quality raw material is suitable for drying, while wilted, overripe, unripe, cracked, or berries affected by diseases or pests are not suitable for drying.

Based on results of cranberry tasting evaluation, the flavor profile of "Black Veil" fresh cranberries received high ratings across all parameters, with a score of 5.0 for taste, aroma, and external appearance, and 4.5 for color and consistency. The flavor profile is described as "Sweet and sour".

"Washington" fresh cranberries also received high ratings, with a score of 4.5 for taste and color, and 5.0 for aroma, consistency, and external appearance. The flavor profile is described as "Sweet-sour".

In comparison, the dried "Black Veil" cranberries received slightly lower ratings across all parameters, with a score of 3.8 for taste and aroma, 4.0 for color and consistency, and 3.8 for external appearance. The flavor profile is described as "Sweet".

Similarly (**Fig. 2.1**), the dried "Washington" cranberries also received slightly lower ratings compared to the fresh ones, with a score of 4.0 for taste, 4.1 for aroma, 3.8 for color, 4.0 for consistency, and 3.5 for external appearance. The flavor profile is described as "Sweet".

Table 2.2 Results of cranberry tasting evaluation

Variety	Evaluation on a 5-point scale					Flavor profile
	Taste	Aroma	Color	Consistency	External Appearance	
Black Veil	5.0	5.0	4.5	4.8	5.0	Sweet and sour
Washington	4.5	5.0	4.8	4.5	5.0	Sweet-sour
Dried Black Veil	3.8	4.0	4.0	4.1	3.8	Sweet
Dried Washington	4.0	4.1	3.8	4.0	3.5	Sweet

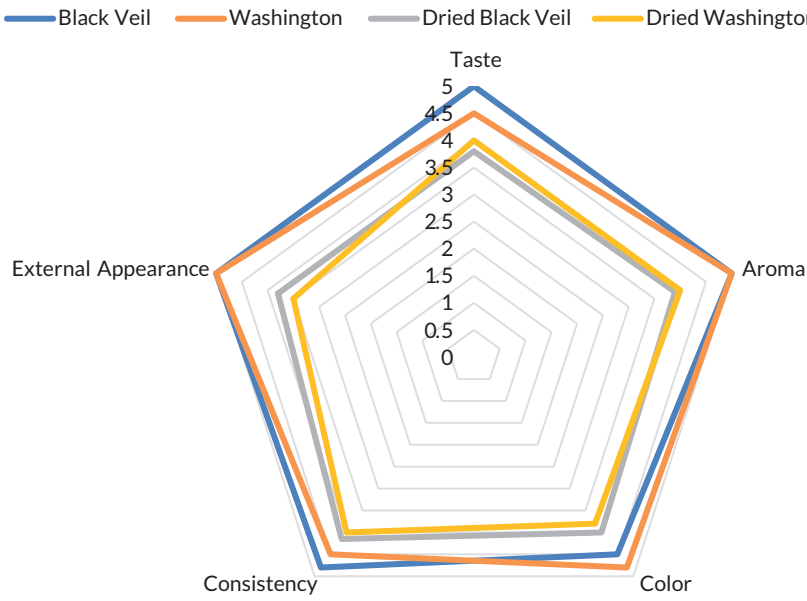

Fig. 2.1 Results of organoleptic evaluation of fresh and dried cranberries

Dried cranberries stand out with an attractive appearance, non-sticky berries, a sweet taste, and rich aroma. It was not possible to determine a preference for a particular variety because both varieties have excellent taste and an elastic, unbroken structure after the sublimation drying process, indicating the preservation of quality indicators and the ability for transportation and storage of the final product.

During the study of the antioxidant properties of cranberries, the presence and content of biologically active compounds in the berry were identified and determined (**Table 2.3**).

Dried cranberries contain a higher concentration of procyanidins compared to fresh ones (0.36 % vs. 0.14 %). This suggests that the drying process may result in the concentration of procyanidins in cranberries. Both fresh and dried cranberries contain phenolic compounds, with dried cranberries having a slightly higher content (1.32 % vs. 1.16 %). Similar to phenolic compounds, dried cranberries have a higher concentration of polyphenolic compounds compared to fresh ones (0.92 % vs. 0.48 %). Overall, the drying process affects the concentration of various antioxidant compounds in cranberries, with some compounds being concentrated while others are reduced.

Table 2.3 Content of biologically active compounds in cranberries

Quantitative contents	Based on absolutely dry raw material ($m=5$), %	
	Fresh Cranberries	Sublimated (dried) Cranberries
Anthocyanins	0.23±0.01	0.16±0.01
Procyanidins	0.14±0.01	0.36±0.01
Phenolic compounds	1.16±0.01	1.32±0.01
Polyphenolic compounds	0.48±0.01	0.92±0.01

The biochemical composition of dried cranberry products contains a significant amount of compounds with biological activity. Phenolic compounds such as anthocyanins, leucoanthocyanins, and catechins contribute to increased enzyme activity and improved elasticity of blood vessels. Pectins found in cranberries form strong compounds with heavy and radioactive metals, aiding in their removal from the body.

Based on the results of conducted research, it can be concluded that freeze-dried cranberries retain biologically active compounds at a high level. Therefore, cranberries are a very beneficial fruit, possessing anti-inflammatory, antibacterial, hypotensive, immunomodulatory, antioxidant, antiviral, and cytotoxic properties.

Berry snacks in the form of pastilles are becoming increasingly popular due to their high content of vitamins, minerals, and antioxidants, as well as their low saturated fat and cholesterol compared to traditional meat or dairy snacks. Cranberry pastille is a special type of confectionery made from puree, sugar, and gelatin. It has a smooth texture and sweet taste, containing vitamins and beneficial substances. Pastille can be enjoyed as a dessert or simply as a tasty and healthy low-calorie snack.

The energy value, or caloric content, is the amount of energy produced during the biological oxidation of fats, proteins, and carbohydrates contained in the raw material, expressed in kilocalories (kcal) or kilojoules (kJ).

According to the chemical composition, fresh cranberries contain on average: fat – 0 g, protein – 0.5 g, carbohydrates – 4.8 g, while in dried cranberries, respectively: fat – 0.16 g, protein – 0.38 g, carbohydrates – 8.2 g.

To determine the theoretical caloric content, we considered the energy value coefficient of nutrients and their content in cranberries. Therefore, for fresh cranberries, the theoretical caloric content is: 2.0 kcal (carbohydrates)+18.0 kcal (proteins)= =20.0 kcal; for dried cranberries, the theoretical caloric content is: 1.44 kcal (carbohydrates)+1.52 kcal (proteins)+30.75 kcal (carbohydrates)=33.71 kcal.

Knowing the theoretical caloric content, we determined the actual caloric content taking into account digestibility, expressed as the digestibility coefficient.

For mixed nutrition, the digestibility is: 84.5 % for proteins, 94 % for fats, and 95.6 % for carbohydrates.

For fresh cranberries:

(2.0·84.5)/100+(18·95.6)/100 = 18.9 kcal.

For dried cranberries:

(1.44·94.0)/100+(1.52·84.5)/100+(30.75·95.6)/100 = 32.04 kcal.

Therefore, the actual caloric content per 100 grams of fresh cranberries is 18.9 kcal, and for dried cranberries, it is 32.04 kcal, taking into account the digestibility coefficient.

To obtain the energy value in the International System of Units (SI), which is kilojoules, we used the conversion factor: 1 calorie = 4.186 kilojoules. Therefore, the energy value of fresh cranberries was 18.9 calories (79.19 kilojoules), and for dried cranberries, it was 32.04 calories (134.25 kilojoules) per 100 grams of edible portion.

Conclusions

The benefits of using the sublimation method for preserving the antioxidant properties of cranberries have been studied. Cranberries are known for their antioxidant properties, which help combat infections, reduce the risk of heart disease, and improve arterial pressure. This berry is particularly beneficial in prostate cancer.

Most of the beneficial compounds in cranberries are found in their skin, which may lose its properties during traditional juice extraction. Drying is an alternative method for preserving antioxidants, but traditional methods can lead to a loss of product quality.

Sublimation drying has proven to be the most efficient and innovative method, as it ensures the preservation of cranberry antioxidant properties. After the sublimation cycle, the final moisture content of the material is only 2–5 % of the initial content, guaranteeing the maximum retention of beneficial properties and the production of a high-quality product. This method is promising for maintaining the quality of raw materials during drying and preserving their medicinal properties.

The obtained results indicate that the application of sublimation drying allows preserving the bioactive compounds and quality indicators in cranberries. The excellent sweet taste and rich delicate aroma of the berries remain even after the drying

process. The caloric content of dried cranberries is approximately 32 calories per 100 grams of berries.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 3

Analysis of the hypotheses of milk fat phase dispersion and structural features of homogenizers

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Abstract

We have carried out the analysis of hypotheses, mechanisms, prevailing hydrodynamic factors of the milk emulsion fat phase dispersion, hydrodynamic conditions of milk fat globules disruption in the modern designs of dispergators and methods of analysis of the equipment for micro emulsions homogenization.

It points out a wide range of designs of homogenizers and a large number of existing hypotheses of milk emulsion dispergating that contradict each other.

Despite substantial differences, the general features of designs which allow receiving a high degree of dispergating is to create hydrodynamic conditions to provide increasing relative velocity of movement of the fat globule and acceleration of the emulsion stream.

Analysis of methods of intensifying the dispergating process of milk emulsions resulted into distinguishing prospective ways to increase energy efficiency of homogenizers and designs with the biggest potential for diminishing energy consumption.

Keywords

Milk homogenization, hydrodynamic factors of emulsions dispersion, design analysis of homogenizers, principle of homogenizer action, homogenization hypotheses, classification of homogenizers, mechanisms of milk fat globules disruption, homogenization intensification methods.

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3.1 Introduction

The milk homogenization is understood as the process of its processing which leads to the dispersion of the fat (dispersed) phase and its uniform distribution over the volume of the dispersed phase [1].

Today, the vast majority of milk as a raw material for the production of drinking milk, cream and other types of dairy products is subjected to homogenization. The main advantages of products produced using homogenization are given in **Table 3.1** [1, 2].

Table 3.1 Advantages of homogenized dairy products

Type of dairy products	Advantages of the product after homogenization
Whole milk after milking	Reduction of the development of oxidation processes, destabilization and whipping during intensive mixing and transportation
Pasteurized milk and cream	Providing uniformity of color, taste, fatness. Improving the consistency, increasing the intensity of white color. Reduction of fat film during boiling, which preserves milk solids. Increase in digestibility (homogenized milk corresponds to boiled milk in terms of fat digestion)
Sterilized milk and cream	Increased stability during storage. Reduction of fat deposition
Sour milk products (sour cream, kefir, yogurt, etc.)	Increasing the clot strength, stability and improving the consistency of protein clots, increasing the viscosity, reducing the whey secretion
Canned condensed milk	Prevention of the separation of the fat phase during long-term storage
Dry whole milk	A decrease in the amount of free milk fat, not protected by protein shells, which leads to its rapid oxidation under the influence of atmospheric oxygen
Reconstituted milk, cream and fermented milk drinks	Better taste of the product and prevention of the appearance of a watery aftertaste
Milk with fillers	Improves taste, increases viscosity and reduces the likelihood of sediment formation
Some hard cheeses	Facilitating the access of mold lipases to milk fat during cheese ripening
Some cheeses from recombined milk and some fresh fermented milk cheeses (creamy, etc.)	Preventing the deposition of a fat layer during a relatively long period of gel formation, contributing to the improvement of product homogeneity, as well as the formation of a loose and brittle texture
Milk mixtures for the ice cream production	Improvement of whipping of mixtures for the ice cream production, its structure and homogeneity

In addition to the dairy industry, the preparation of highly dispersed emulsions, which are stable for a long time, is widely used in the preparation of:

– mixtures for ice cream (preparation of the mixture "milk base – vegetable fat");

– mayonnaise, margarine, ketchup, etc. products;

– non-stick emulsions (layers) for greasing bread molds and sheets;

– emulsions for surface treatment of agricultural products – creation of a film-forming protective layer on their surface;

– cooked sausages, when raw fat is added to the minced meat in the form of a water-fat emulsion;

– dough when emulsion is introduced instead of fat, thanks to which up to 90 % of fat is preserved;

– cosmetic and pharmacological preparations, in which emulsions are absorbed faster by the body, soften the irritating effect of the ingredients;

– medicinal oils that lose unpleasant taste and smell;

– obtaining an emulsion based on the use of skimmed milk by adding fat and other necessary ingredients during the production of whole milk substitutes.

In addition to the advantages, the homogenization of dairy products also has disadvantages:

– increase in the cost of the product;

– increased sensitivity to light, which leads to taste defects, such as rancidity, soapiness and oxidation;

– milk becomes unsuitable for the production of many types of hard cheeses, due to too soft coagulation and difficulty in releasing moisture;

– whole milk is not suitable for homogenization due to the rapid deterioration of the aroma due to the action of lipase.

3.2 Properties of milk emulsion as an object of hydrodynamic dispersion and homogenization

The dispersion phase of milk emulsion is milk plasma, which is a solution of milk sugar and salts in water. Some authors [3, 4] distinguish a third phase of milk – the protein phase, consisting mainly of insoluble casein micelles and submicelles, as well as whey proteins.

Special attention is not paid to the uniformity of the distribution of microscopic fat particles due to their constant (Brownian) motion, due to which the fat concentration in the microvolume of the milk emulsion is equalized without applying special means and conditions.

The fat phase of milk is milk fat in the form of fat globules (droplets, particles), the size of which in whole milk ranges from 0.1 to 10 μm.

The majority of fat globules in such milk is 2–6 μm in size, and their average size is 2–4 μm.

The number of fat globules in raw milk is 1.5–3.0 billion in 1 ml.

In the process of homogenization, the average diameter of fat globules decreases to 0.75–1.2 μm, while the number of fat globules increases to 40–80 billion in 1 ml, and the surface area of fat globules increases 13–27 times.

There are no standards and regulations regulating the dispersion degree of milk fat particles after homogenization. The only homogenization standard is GOST 27203-87 "Gomogenizatory dlya moloka. Osnovnyie parametry" (State standard of USSR 27203-87 "Homogenizers for milk. Main parameters"), which regulates only the main technical parameters of plunger homogenizers of the valve type without taking into account the degree of dispersity of milk fat after processing (currently not active).

To determine the sufficient dispersion of the fat phase after homogenization, there are the following guidelines:

– the chemical control instruction, in which it is recommended to check the quality of homogenization by settling the fat for 48 hours or by the centrifugation method, and it is stated that the method of microscopic determination of the size of fat globules is considered the most reliable;

– the average size of fat globules in the most common valve homogenizers, which reaches 0.75–0.80 μm at operating modes aimed at the maximum dispersion degree [1, 3];

– the average size of fat globules after processing in valve homogenizers according to the recommended modes of homogenization (pressure) in technological schemes for the production of drinking milk and cream, which is considered sufficient, is 1.0–1.2 μm [2];

– the lower limit of dispersion of milk fat emulsion after processing in serial but less common types of homogenizers (vacuum, rotary-pulsating, etc.) is 1.0–1.2 μm [3, 4];

– in accordance with the United States Public Health Service, in well-homogenized milk, there is no visible settling of cream within 48 hours;

– the fat content in the top 100 ml of a 250 ml bottle should not differ by more than 10 % from the milk in the rest of the bottle.

Thus, it can be considered that the dispersion of the milk emulsion is high when the average size of the fat globules is 0.75–0.8 μm and less, and sufficient when the average diameter is 1.2 μm.

3.3 Analysis of the dispersion hypotheses of the fat phase of milk

Dispersion consists of two stages: deformation of the fat globule and its disruption. After dispersion, the newly formed fat globule must be stabilized. Otherwise, the process of its coalescence may occur.

The process of deformation and disruption of milk fat globules is difficult to study experimentally (**Table 3.2**).

Table 3.2 The main reasons for the difficulties in obtaining visual data on the disruption of fat globules of milk during homogenization

The main reasons	A possible way to solve the problem
High velocities of movement of fat globules (up to 200 m/s)	High-velocity filming
Microscopic dimensions of fat globules (0.1–5 μm)	Optical or electron microscopy
Low transparency of milk emulsion	Special dyes
There is little difference in the density of milk plasma and milk fat	
The need to place the objective of the optical microscope at a distance of less than 1 mm from the object of study	Performance of the objective as a part of the working body of the homogenizer
The large length of the disruption zones of fat globules relative to their size (3 orders of magnitude larger than the diameter of the fat globule)	Use of pulsed microlasers

The lack of necessary experimental data led to the appearance of many hypotheses of the dispersion mechanism of the fat phase of milk (homogenization), the main ones of which are presented in **Table 3.3**.

Let's consider the essence and reliability of most theories using the example of the most studied valve homogenizers, which have the highest dispersion degree. The disruption of the fat globule in the valve homogenizer occurs in the gap between the valve and the seat of the homogenizing head, the size of which is 0.3–1.5 mm. The milk supply pressure is 10–25 MPa, as a result of which the velocity of milk in the valve gap reaches 150–200 m/s.

Criticism of the hypothesis of the disruption of fat globules by Prof. Baranovsky, which appeared in the 50s of the last century, is presented in many works [5] and is confirmed by the latest data [6]. The essence of the theory is that a fat globule of milk, moving towards the valve gap, with dimensions d at a flow rate υ_0 at a plasma pressure p_0, is pulled out at the entrance to the valve gap, with a height h where its

velocity increases significantly to υ_m at a pressure p_1, and then disintegrates under the action of surface tension forces (**Fig. 3.1**).

Table 3.3 Basic hypotheses of the milk homogenization mechanism

The essence of the hypothesis	The authors of the hypothesis
The disruption of fat globules under the influence of the longitudinal gradient of the flow velocity at the entrance to the valve gap	M. V. Baranovsky
Disruption under the influence of the transverse gradient of the flow velocity	P. O. Rebinder, H. Wittig
Disruption due to centrifugal force during rotation of a fat globule	V. D. Surkov
Disruption due to Kolmogorov-Khintse turbulence	Kolmogorov-Khintse
Disruption due to cavitation	A. A. McKillop, H. A. Kardashev, A. N. Tkachenko and others
Disruption of microparticles by blowing from the surface of a fat globule during impulse effects on the emulsion	M. M. Oreshyna
Disruption due to low-temperature cavitation homogenization	E. A. Fialkova
Disruption by boiling of microvolumes of emulsion in a vacuum	A. A. Dolynskyi
Disruption due to the velocity difference between the fat globule and the dispersion medium in the jet collision zone	K. O. Samoichuk

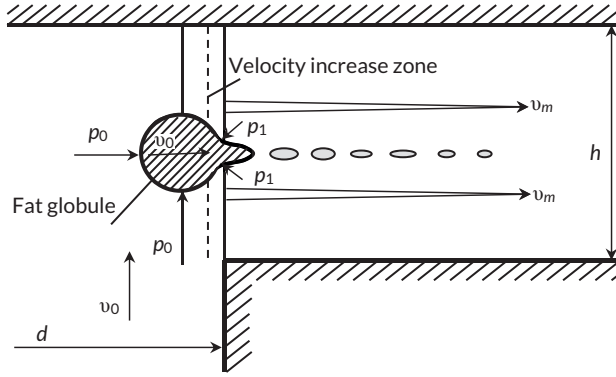

Fig. 3.1 The scheme of homogenization according to the Prof. Baranovsky's theory

The main arguments of the opponents of this theory: the actual scale of the process, where the dimensions of the fat globule are 1–2 orders of magnitude smaller

than the size of the valve gap, the impossibility of obtaining a significant difference in velocity over a length comparable to the dimensions of the fat globule (1–3 μm), etc. Calculations of the theoretically possible conditions for crushing a fat globule according to this hypothesis in a valve (the most widespread and studied) homogenizer showed that the necessary pressure drop for the disruption of a fat globule is created only under the condition of entering the valve gap at an angle of 68°, which is unlikely.

H. Wittig proposed to consider the initial fat globule before homogenization as "mother" consisting of several fat particles (**Fig. 3.2**).

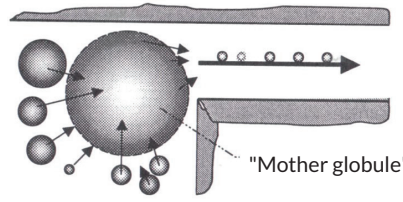

Fig. 3.2 Scheme of the "Mother globule" formation according to Wittig's hypothesis

Thus, the contradiction between the non-observance of the scale between the sizes of the fat globule and the valve gap in Baranovsky's theory was avoided. But, if to agree with this point of view, then the presence of a stagnant zone is necessary, in which the fat globules would merge and form the maternal one. Experiments with the flow of liquid in the gap between the valve and the seat did not confirm the presence of such a zone. In addition, if such a zone existed, the eddy current that would form in this zone would prevent the formation of the mother globule [7].

According to Rebinder's hypothesis (subsequently this theory was also put forward by Wittig) the reason for the deformation and disruption of fat globules of milk is considered to be a large gradient of milk movement velocity in the homogenizing gap of the valve homogenizer. Under the influence of forces acting from the side of the flow, fat globules are stretched into cylinders or threads, overcoming the forces of surface tension and entering an unstable state, and then, under the influence of the same forces of surface tension, they break up into smaller ones. Rebinder established that the disintegration of globules occurs when the ratio of the length of the cylinder to the diameter is equal to or greater than π.

According to the calculations of the conditions created in the valve homogenizer, only half of the fat globules passing through the valve gap can perceive the stretching effect of the velocity gradient (**Fig. 3.3**). The rest of the fat globules pass through the central part of the flow, where the velocity gradient is insufficient for dispersion.

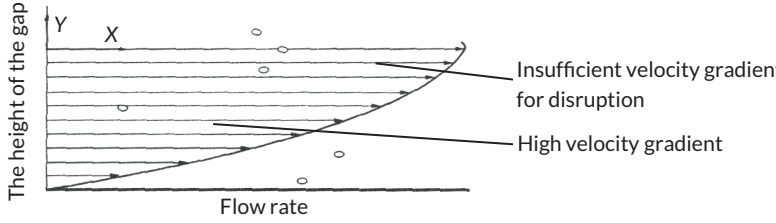

Fig. 3.3 Field of flow velocities in the valve gap of the A1-OG2S homogenizer

Prof. V. D. Surkov suggested that the fat globules should rotate and disintegrate due to centrifugal force in the slit channel. His hypothesis is based on the action of the transverse velocity gradient in the flow, which has different velocities in the cross section. According to this theory, a torque caused by the difference in velocities is applied to the surface of the globule, which is at the boundary of the layers.

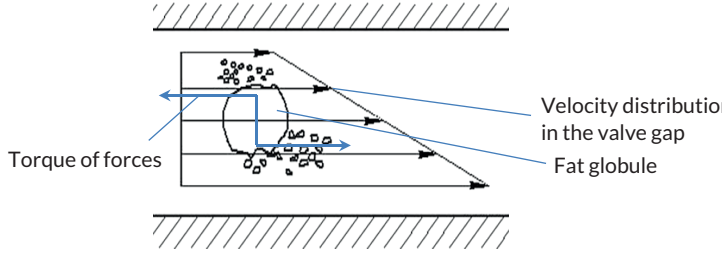

Fig. 3.4 Dispersion of a fat globule according to V. D. Surkov

Under the influence of this moment, each globule, which performs a rotational movement, loses its initial shape, then the centrifugal forces increase, become greater than the forces of surface tension, after which the globule disintegrates into smaller ones. According to this theory, the laminar flow mode in the valve gap is most suitable, which is refuted by experimental studies. Calculations show that half of the fat particles that pass through the central part of the valve gap, where the velocity gradient is small, cannot be destroyed according to the theory of centrifugal disruption.

The hypothesis about the predominant influence of cavitation as the main factor in the homogenization process developed in leaps and bounds: from the main one for valve homogenization to a minor and not influential one [4]. Evidence of cavitation in the valve gap is erosive annular formations on the working surfaces of the seat and valve. But first by M. V. Baranovsky, and later by other researchers, it was experimentally proven that the intensity of cavitation does not affect the homogenization

degree, and strongly deformed fat globules pass through the cavitation zone in the initial part of the valve gap intact, and are destroyed much later. Experiments [8] established that the intensity of cavitation in the valve gap is small, in contrast to the exit from the valve gap, where cavitation occurs much more intensively.

Cavitation disintegration, as the main factor of dispersion, develops in two directions: hydrodynamic and acoustic, the mechanism of influence of which on the dispersion of the dispersed phase of the emulsion does not differ.

According to Tkachenko's hypothesis, pulsating cavitation bubbles appear in the cavitation zone and collapse upon contact with droplets of the dispersed phase. Cumulative jets formed in bubbles hit the fat globule and break it into smaller ones.

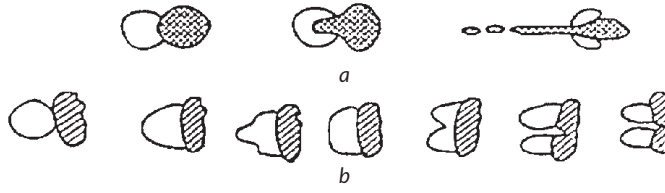

Fig. 3.5 Scheme of the cavitation dispersion process:
a – pulling a fat drop into a bubble; *b* – disruption of a fat droplet of a dispersed phase

According to the principle described above, for the disruption of a fat globule, the coincidence in space and time of at least two factors is necessary:

– the presence of a fat drop in the immediate vicinity of the cavitation bubble;

– the location of the fat drop on the side of the appearance of the cumulative jet.

Such a coincidence of conditions is possible only with a large multiplicity of processing of one volume of emulsion or long-term processing.

Another, and more likely, mechanism of cavitation is the dispersion of the fat phase due to high local pressure differences (shock waves) during the collapse of cavitation bubbles (**Fig. 3.6**).

In the zone of local high pressure around the collapsing cavitation bubble, the pressure reaches 1000 MPa. In addition to hydraulic shock, the temperature rises significantly and hydrogen is released, the presence of which worsens the properties of milk.

The appearance of local high-velocity zones leads to the appearance of high accelerations of microvolumes, which leads to a high velocity of sliding of fat globules relative to the plasma and to their disruption according to the Weber's criterion. In this case, the sliding velocity during cavitation is most affected by the size of the cavitation bubbles and their concentration. It was found [4] that in order to increase

the dispersion degree of the fat phase, it is necessary to reduce the size of the cavitation bubbles, which occurs with an increase in the flow rate in the cavitation zone (increase in the Reynolds number), which coincides with the dependence of the dispersion of the fat phase of milk on the flow rate in the valve gap. This may be indirect evidence of disruption due to the sliding velocity of the fat globule.

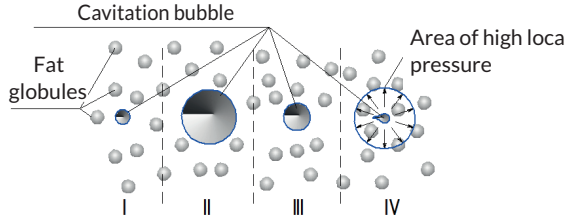

Fig. 3.6 The scheme of the disruption of fat globules during cavitation:
I – formation of a cavitation bubble; II – reaching the maximum size of the bubble;
III – decrease in size; IV – explosion of the bubble with the formation of a cumulative jet

With cavitation dispersion, the effect of cavitation on the dispersion degree of the emulsion gradually decreases during repeated processing until the moment when dispersion stops due to cavitation. Experiments showed that the minimum size of fat globules due to cavitation reaches only 1.4–2.0 μm. An industrial plant for cavitation milk homogenization will have a low productivity (less than 500–1000 l/h), with an average emulsion dispersion of 2.0 μm and energy consumption much higher than valve machines (20 J/cm^3) at a higher cost of the device.

Thanks to the theory of cavitation, the fact that when cavitation appears, the relation between the homogenization degree and energy consumption changes significantly: with the same supplied energy, homogenization becomes more effective. Homogenization in the valve gap can be organized without cavitation, but this reduces the efficiency of the process.

Taking into account the results of cavitation research, this process can only be an additional intensifying factor for the milk homogenization if it is necessary to obtain highly dispersed emulsions (<1 μm), and the cavitation mechanism of disintegration can be explained by the occurrence of a high sliding velocity during the explosion of cavitation bubbles in milk.

A. N. Kolmogorov and I. O. Khintze presented theories of turbulent dispersion of drops: isotropic and viscous (**Fig. 3.7**).

According to the mechanism of isotropic turbulence, dispersion occurs due to pressure fluctuations caused by microvortices. In the case of a viscous mechanism –

shear stresses of larger-scale vortices. The turbulent homogenization mechanism is the main one compared to the gradient hypotheses of dispersion and cavitation dispersion. According to Kolmogorov's hypothesis, the size of hydraulic vortices determines the dispersion of the emulsion: the smaller the size of the vortices, the smaller the size of fat droplets. And the size of microvortices decreases with increasing flow velocity.

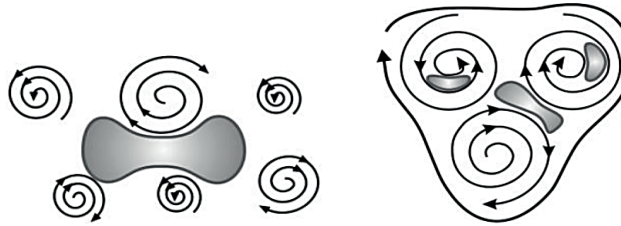

Fig. 3.7 Schematic presentation of turbulent dispersion mechanisms: *a* – isotropic; *b* – viscous

According to the Kolmogorov-Khintse theory, the following can destroy a drop: dynamic pressure and the force of viscous friction. Depending on which of the forces acting on the surface of the drop dominates, two mechanisms of drop disruption are possible. The main factor that determines the dynamic pressure is the velocity of the external medium relative to the droplet (sliding velocity). The average shear rate and specific energy dissipation are decisive for the force of viscous friction. Later, Sleicher proved in visual experiments based on the results of high-velocity photography that:

– the main parameter for the disruption of a fat drop is velocity;

– the Kolmogorov-Khintse theory of isotropic turbulence cannot be used to disrupt droplets in a flow where there is a high velocity gradient;

– the most frequent mechanism of disruption is the pulling out of drops, and when the ratio of their length to the diameter is greater than 4, several new small drops are formed, and when the ratio is less than 4, only two new drops are formed.

Thus, according to the theory of turbulence, it was experimentally proven by visual observations of the disruption of a drop during its extraction according to the viscous mechanism, the main factor of which is the drop velocity. In 2005, these conclusions were confirmed experimentally for the valve gap [8].

The maximum size of droplets formed during crushing in the flow of a continuous medium is determined mainly by three mechanisms:

– Kelvin-Helmholtz instability, which is determined by the value of the relative velocity;

– Rayleigh-Taylor instability determined by the acceleration value;

– the mechanism of disruption by A. N. Kolmogorov's turbulent pulsations, determined by the magnitude of power dissipation.

Therefore, in order to find out the predominant mechanism of the dispersion of the fat phase in the valve gap of the high-pressure homogenizer, thorough studies of the velocity fields of microparticles were carried out using the most modern methods of pulsed lasers [8]. Experiments have shown that cavitation is concentrated in the first half of the valve gap, while the intensity of turbulence in this place is very low. Turbulence is most effective in the exhaust chamber after the valve gap. This confirms the formation in this place of the chamber of turbulent eddies with dimensions comparable to fat globules, which are known to be the most effective for disruption. High turbulence in the last part of the valve gap leads to an increase in the energy of large turbulent eddies and a decrease in the energy of small eddies. This will mean a relative increase in the influence of the turbulent viscous mechanism of disruption in comparison with the turbulent inertial mechanism when dispersity increases. Comparing these findings with the visualization of the dispersion process, turbulence, to a greater extent than cavitation, is the dominant factor in homogenization in the valve gap.

Thus, to date, the predominant effect of the viscous turbulent mechanism of milk homogenization in the valve gap has been experimentally confirmed. Cavitation plays a secondary role, but increases the dispersion efficiency.

E. A. Fialkova puts forward the hypothesis of low-temperature cavitation homogenization or vitrification of fat globules of milk in the process of dispersion, which is based on the idea of the formation of "micro-icicles" on the sub-cavitation surface of cavitation bubbles, formed as a result of sublimation and destroying both the fat globules and the working surface of the valves [9].

According to this theory, in the high-velocity zones of homogenizers, the liquid pressure decreases to such values that sublimation of the surface layer of fat globules occurs due to low temperatures, i.e., their transition into a solid state (**Fig. 3.8**). During further movement, microscopic particles of ice moving at high velocity crush the fat globules.

The author believes that dispersion in the valve homogenizer occurs precisely according to this theory and confirms the pressure distribution in the valve gap experimentally studied by Katsnelson and Mukhin, where the ultra-low pressure zone is shown [9].

The time of presence of a fat globule in the valve gap is only $(1–2)\cdot10^{-5}$ s. The author did not calculate the freezing rate of the surface layer of fat globules in such a short time. Experiments did not confirm the idea of vitrification of fat globules.

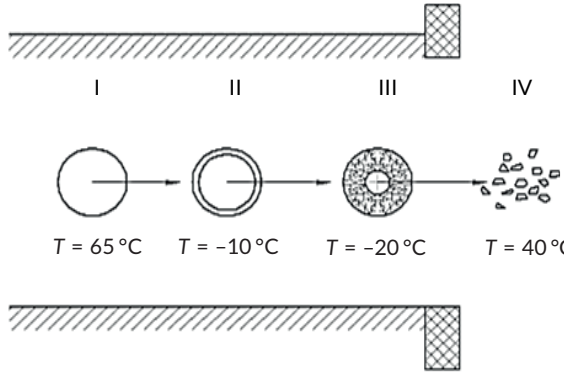

Fig. 3.8 Stages of a fat globule crushing according to Prof. E. A. Fialkova

In the early 2000s, a class of vacuum homogenizers was introduced that was developed on the basis of research by the Institute of Technical Thermal Physics of the National Academy of Sciences of Ukraine. The principle of their operation is in injecting milk heated to 60 °C through a nozzle into a chamber where a vacuum is maintained. The depth of the vacuum is calculated in such a way that the milk drops boil, due to which the fat globules are destroyed. A fundamentally new principle of homogenization provides such advantages as deodorization and reduction of milk acidity. However, in vacuum homogenizers, it was not possible to reduce the average size of milk fat globules to 1.2 μm.

The homogenization theory by boiling microvolumes of emulsion in a vacuum is fundamentally different from other dispersion methods and can only be applied to vacuum homogenizers.

If to compare the theories of M. V. Baranovsky, A. N. Tkachenko, H. Wittig and E. A. Fialkova, the influential factor in all cases will be the velocity of the flow. Indeed, Baranovsky proved that the homogenization degree is affected only by the velocity of the liquid flow. When the flow rate increases through the valve gap, the amount of vacuum will increase and, as a result, cavitation, which is the driving force of homogenization according to the cavitation theory and the theory of Fialkova. At the same time, the velocity gradient increases, which is the cause of disruption according to Rebinder and Wittig. This once again confirms that the factors of the homogenization process and the lack of visual data about it can lead to significant discrepancies and errors in the explanation of its mechanisms and driving forces.

Thus, over the past 60 years, a huge amount of experimental material on homogenization research in valve machines has been accumulated, but it has not yet been

possible to directly observe the disruption of fat globules. A breakthrough in this direction was the research of Dr. Frederick Innings at the University of Lund (Sweden). A sapphire window with pulsing lasers along the lumen was created in the homogenizing head, which made it possible to observe the sequence of the fat globule splitting process and photograph it with high-velocity cameras. As a result, it was concluded that fat globules are deformed under the action of acceleration upon entering the gap and pass through it in such a deformed state in an elongated form. Separation occurs only under the influence of turbulent flows, when the globules go outside. It is the velocity gradient – the phenomenon of the difference in velocity of movement of different parts of the stretched globules – that ensures its disruption.

The hypothesis of disrupting a fat globule by blowing microparticles from its surface was put forward by M. M. Oreshyna and then developed by N. A. Palianychka and K. O. Samoichuk [10]. A fat globule is considered like a drop of liquid that is crushed in a high-velocity air stream. The crushing mechanism is based on the breakup of the drop depending on the difference in velocity of the fat globule and its surrounding plasma (sliding velocity), which determines the Weber's criterion (**Fig. 3.9**).

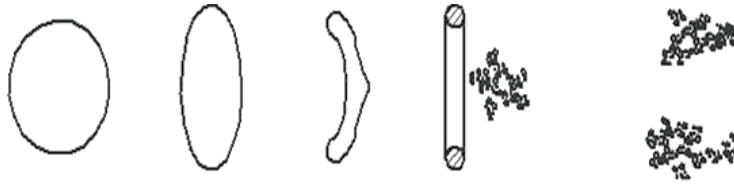

Fig. 3.9 Homogenization scheme according to Prof. M. M. Oreshyna

The mathematical model of the crushing of fat globules by hydraulic disturbances is based on the hypothesis that the dispersion medium captures the fat globule in motion and, taking this into account, the relative movement of the medium and the particle is formed. The significant role of the acceleration of the fat globule was highlighted [11, 12].

The downward or upward movement of the impactor piston causes the dispersion phase to move at a velocity υ_{pl}, which flows around the fat globule moving in the opposite direction due to the inertial force F_i (**Fig. 3.10**) [10].

Experiments on the deformation and disruption of liquid droplets during air flow, carried out in work [9], made it possible to obtain photographs of the disruption and to highlight several characteristics of the disintegration of the globules

depending on the Weber's criterion. For M. M. Oreshyna it was possible to obtain photographs of the disruption of an oil droplet in a water flow by pulsed effects, which simulates the characteristics of a fat globule in a plasma flow. According to the author, the size of fat globules of milk after processing in the developed pulse homogenizer is smaller than when processing in valve homogenizers and, on average, is 0.5 μm.

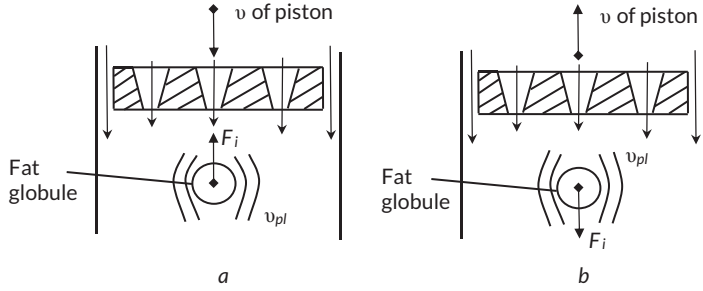

Fig. 3.10 The scheme of the emergence of inertial forces during impulse homogenization during the movement of the impactor piston: *a* – down; *b* – up

The fat globule has a complex structure: milk fat globules are covered with a thin protein-lipid shell, under which is a layer of refractory fats. Such a resilient and at the same time elastic shell creates additional difficulties in crushing the fat globule. In addition, after its disruption, shells are formed again on the surface of new, smaller fat globules, which prevent the process of their agglomeration, which also takes time. If the complex internal structure of the fat globule is neglected, then the view of the process of its crushing will be too simplified and will not correspond to reality. In view of this, a drop of oil in the experiments of M. M. Oreshyna cannot be considered an adequate model of the fat globule of milk.

A small difference between the density of the plasma and the fat globule creates a significant involvement of the movement of the adjacent layers of milk. Therefore, the direct transfer of the mechanisms of liquid grinding in the air stream, where the difference in density differs by almost 3 orders of magnitude, to the grinding of the fat globule in the milk plasma is doubtful. Despite this, the high dispersion degree of the fat phase of milk in the pulse homogenizer allows to conclude that the mechanism of dispersion due to the sliding velocity of the fat globule is promising for further research.

To create the maximum sliding velocity of the fat globule, the homogenization theory during the collision of milk jets was suggested [13]. In the collision zone of

the jets, the fat globule, due to the forces of inertia, moves in a straight line with the velocity υ_1 (**Fig. 3.11**), while the velocity of the surrounding plasma υ_2 changes the direction of movement first by 90° and then by 180°. For some time, the fat globule moves in in the counter-jet flow, where the maximum sliding velocity of the fat globule is created, which leads to its disruption in accordance with the Weber's criterion, modified for the case of counter-jet homogenization.

When processed in a counter-jet homogenizer, the sizes of fat globules are comparable or smaller than their sizes during valve homogenization, however, visual observation of the dispersion process was not obtained.

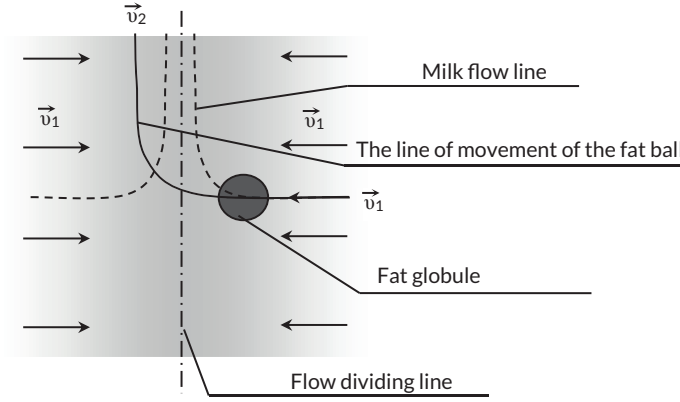

Fig. 3.11 Scheme of homogenization in the collision zone of jets of a counter-jet homogenizer

As a result of the conducted analysis, it is clear that a significant number of homogenization hypotheses are caused by difficulties in obtaining visual data of the disruption of fat globules. Recent studies of the process of dispersion of the fat phase in valve homogenizers indicate a strong stretching of fat globules in the valve gap before disruption and confirm the validity of the turbulent viscosity theory, according to which disruption occurs as a result of Kelvin-Helmholtz and Rayleigh-Taylor destabilization. Such globule disruption mechanisms are caused by the velocity and acceleration of the emulsion flow. Cavitation intensifies the valve homogenization process, but its effect is secondary.

A high degree of dispersity of the fat phase of milk is achieved when using devices built on the hypotheses of blowing the surface of microparticles and the difference in velocity in the collision zone of the jets. The commonality between these

hypotheses is the creation of conditions for the occurrence of the maximum velocity difference between milk phases.

Hypotheses of homogenization by boiling microvolumes of emulsion in a vacuum and sub-cavitation homogenization are fundamentally different from others. The first of them did not receive visual confirmation for the valve homogenizer, and the second is applicable only for vacuum homogenizers, the dispersion degree in which does not reach the level of valve machines.

Despite the significant differences of the hypotheses discussed above, they have in common the creation of hydrodynamic conditions in the disruption zone, which contribute to an increase in the relative velocity of the fat globule. For gradient theories, this occurs at the relative velocity of the emulsion layers, for turbulent disruption – at the formation of microvortices, for cavitation – pressure and velocity pulsations in the collapse zone of cavitation bubbles, blowing of microparticles – movement of the emulsion with high acceleration and sliding of the fat globule relative to the plasma due to inertial forces , for the collision of jets – inertial forces during a sudden change in the plasma movement around the fat globule, for sub-cavitation disruption – alternating zones with low pressure and a high velocity gradient.

3.4 Analysis of structural features of homogenizers and generalization of the predominant hydrodynamic factors of dispersion of emulsions

Dozens of devices are used to carry out dispersion processes and obtain emulsions, which are structurally significantly different from each other. Attempts to classify homogenizers used for milk processing are given in works [1, 5, 7, 9], which are based on both structural features and the principle of action together with hydrodynamic conditions in the grinding zone and the mechanism of fat particle disruption. The combination of several features for classification leads to uncertainty, which is exacerbated by the fact that for many types of homogenizers there is no certainty either in the type of the predominant mechanism of dispersion, or in the hydrodynamic conditions in the grinding zone. Classification according to the most defined – constructive signs allows avoiding the above-mentioned contradictions (**Fig. 3.12**).

Slot (valve) homogenizers. The most common in production are valve-type homogenizers, in which the mixture processed under high pressure (from 8 to 25 MPa) passes through a narrow annular gap (0.1–0.5 mm) formed by a valve and a valve seat (**Fig. 3.13**) [1, 7].

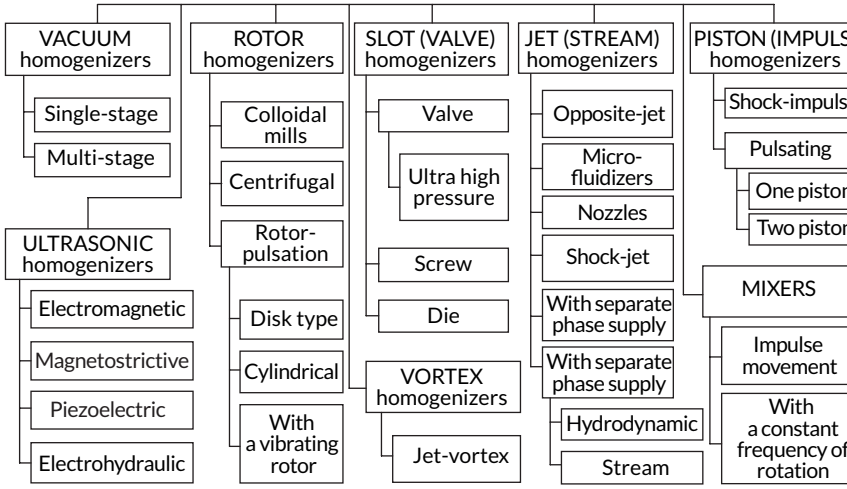

Fig. 3.12 Classification of devices for milk homogenization according to structural features

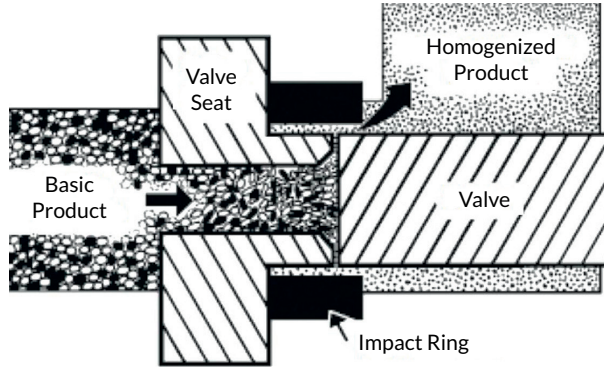

Fig. 3.13 The principle of processing in the valve head of the high-pressure homogenizer

The main advantages of valve homogenizers, due to which they received the highest industrial implementation in the world:

– when processing products, it is possible to obtain highly dispersed emulsions with an average diameter of the dispersed phase of 0.75–0.8 μm;

– insensitivity to obliteration of the working surfaces of the valve and seat due to the "floating" design of the valve;

– versatility, that is, the ability to process milk and cream of different fat content, as well as other products with a wide range of viscosities;

– the vast majority of technological schemes and product production instructions contain recommendations (homogenization modes) developed specifically for valve homogenizers.

Disadvantages of valve homogenizers are significant:

– high cost (more than 120,000 USD at a productivity of 20 t/h);

– the highest, among industrially developed types of machines, energy consumption: 7.4–9 kWh/t, thanks to which the electricity costs for a year of operation reach half the cost of a new machine;

– high mass-dimensional indicators (more than 3 t with a productivity of 10 t/h);

– rapid wear of seals and valves (including cavitation), due to which the cost of maintenance and replacement of worn parts reaches 16,000 EUR/year during milk processing (in the case of homogenization of tomato paste, etc. abrasive products the amount increases significantly);

– the complexity of the design due to the use of a high-pressure plunger pump and high noise level.

Despite numerous improvements of valve homogenizers, the efficiency factor, and therefore the energy efficiency of the homogenization process, remains very low – 0.18 %. At the same time, the mechanical efficiency is quite high (70–85 %), which indicates the imperfection of the homogenization mechanism in valve machines.

Valve homogenizers have the longest history and are characterized by the most research among all other types of dispersers, therefore reliable knowledge of the mechanism of disruption of milk fat globules in this type of homogenizer is key to determining ways to increase the efficiency of homogenization in general. Therefore, let's consider the dispersion process in such a homogenizer in more detail.

The impossibility of observing the milk fat dispersion process led to the emergence of dozens of hypotheses about the possible mechanisms of homogenization in valve homogenizers. Practically each of the hypotheses described in subsection 1.1 was considered the main and predominant one for the valve head of the homogenizer in a certain period of time. But visual experimental data of the process of disruption of fat globules showed that in the valve gap they stretch strongly, pass through the valve gap and break up into small drops at the exit from the working gap.

The obtained results allow to draw the following conclusions:

– visually (stretching into cylinders, with a ratio of length to diameter greater than π), the process coincides with the hypotheses of gradient hypotheses of homogenization;

– hypotheses of disruption due to centrifugal forces (another form of deformation of the fat globule), cavitation, sub-cavitation (which occur only in narrow annular

sections of the valve gap) and blowing of microparticles from the surface (according to which deformation in the form of "parachutes" or "umbrellas" is assumed) do not correspond to reality;

– the disintegration of strongly elongated fat globules at the exit from the valve gap occurs due to turbulent pulsations [14, 15], but cavitation increases the efficiency of this process, because in this part of the valve head there is a zone of intense cavitation [4];

– strong stretching of fat globules (formation of long cylinders) before disruption is consistent with the data of Yu. F. Dityakin and M. S. Volynskyi for dispersing highly viscous emulsions in experiments on the disruption of drops and the theory of turbulent viscous dispersion of Kolmogorov-Khintze.

The last conclusion connects the process of dispersing a fat globule of milk with the well-studied process of liquid droplet disruption, which is determined by Weber's criteria and induction time [12]. Weber's criterion is based on the determination of the difference in velocity of the fat globule relative to the surrounding layer (milk plasma). This velocity is called the sliding velocity of the fat globule. The time of induction of the drop dispersion process, as well as the time of its complete disruption, depends on the Laplace criterion, and therefore on the strength of the surface tension of the drop, the drop size and the emulsion velocity. These factors are decisive in the research of valvular homogenization. Of these, the size of the fat globule before homogenization and its surface tension are constant, and the sliding velocity, which mainly depends on the rate of change of the emulsion velocity (or the velocity gradient, or the acceleration of the emulsion) in the valve gap, and the induction time (the influence of dispersion forces) are variable.

Thus, to increase the dispersion degree in the valve homogenizer, it is necessary:

1) increase the gradient (acceleration) of the velocity, for which increase the homogenization pressure and (or) reduce the length (height) of the valve gap;

2) increase the time the fat globule stays in the valve gap, that is, reduce the flow rate and (or) increase the length of the valve gap.

As it is possible to see, these ways of increasing the homogenization degree in the valve head are in contradiction. Perhaps this is the main drawback of this type of homogenizer. Despite more than a hundred years of existence, a huge amount of research and improvements – attempts to reduce its energy consumption without worsening the quality of dispersion, they actually did not succeed. Modern domestic (Odesa Mechanical Plant) and foreign valve homogenizers (Alfa-Laval, "APV", "Bran&Luebbe", Manton-Gaulin, "Cherry-Burrell", Rannie, etc.) have similar technical characteristics and differ mainly only in the degree of automation and technical perfection of their mechanical part.

Ultra-high pressure homogenizers. Industrial and laboratory valve homogenizers have a structure similar to valve homogenizers, operating at ultra-high pressure (UHP) – from 10 to 300 (1000) MPa [4, 16]. The main differences of the UHP homogenization process:

– dispersion of fat globules reaches 0.1 μm and less;

– in the valve head, the temperature rises to 95 °C, due to which milk is disinfected from pathogenic microflora at the same time as homogenization.

Die homogenizers. In such devices, the product is pushed through parallel holes with a constant or variable cross-section. Such devices are the SVA-3 die device and the MDH401 unit (Unitech&Flant-M, Russia-Bulgaria). In these devices, multi-stage processing takes place, which reduces the required pressure compared to valve homogenizers. During the operation of such devices, the efficiency of homogenization is low and is about 17 %, and when processing for 20 minutes – 20 % [17].

Screw homogenizers. Screw devices operate according to the spinner type, in which the screw and the housing form successively located gaps (the ALM unit by Pierre Guerin) [17]. The product passes through a thin screw channel, which significantly increases the processing time. The dispersion degree of milk in screw homogenizers is higher than in die homogenizers.

Rotary-pulsating (rotor-impulse) devices. A typical design of a radial rotor-pulsating device (RPD) is presented in **Fig. 3.14**.

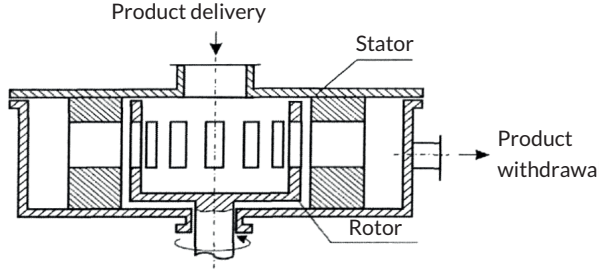

Fig. 3.14 The design of the radial RPD

The working elements of such devices are coaxially arranged cylinders of the rotor and stator, on the side surface of which there are channels for the passage of the processed medium. The part of the RPD, which includes the holes of the rotor and stator, is called the modulator. The principle of RPD operation is as follows [18]. The processed emulsion is introduced into the device through the central nozzle. Passing through the working bodies, the liquid is subjected to significant alternating

loads, as a result of which significant shear stresses arise in it. In addition, high-frequency pulsations and cavitation phenomena act on the mixture processed during RPD operation.

When the rotor rotates, its channels periodically overlap or coincide with the stator channels. In the first case, the pressure in the rotor cavity increases, and in the second case, it is reset in a short period of time. As a result, a pulse of excessive pressure spreads through the stator channel, followed by a short-term pulse of reduced ("negative") pressure, since the combination of the rotor and stator channels is complete and the supply of liquid to the stator channel occurs only due to the transit flow from the radial gap between them. The volume of liquid that has entered the stator channel tends to leave it, and inertial forces create tensile stress in the liquid, which causes cavitation. Cavitation bubbles grow under the action of a pulse of reduced pressure and collapse or pulsate when the pressure in the stator channel increases. Part of the cavitation bubbles is carried into the working chamber.

Since the velocity of the liquid flow in the stator channel is high and is also a variable, the flow is turbulent. The working surfaces of the rotor and stator affect the liquid heterogeneous medium due to high shearing and shearing forces arising in the radial gap and turbulent eddies.

Rotary devices refer to devices with periodic transient hydromechanical processes with the excitation of hydrodynamic and acoustic pulsed cavitation and large velocity gradients and significant pulsations. Transient unstable processes are determined by the fact that the period of modulation of the cross-sectional area is shorter than the time of establishment of the main hydrodynamic parameters: velocity and pressure.

Rotary devices are adapted for autonomous operation with or without an external pressure source. In the first case, a product processed by an external pump is fed through the RPD, which is sometimes technologically convenient. In the second case, the pressure is created under the action of centrifugal forces, and to increase the pumping effect, vanes (similar to centrifugal pumps) or a screw-type pre-pump are installed inside the rotor.

According to the method of processing and movement, RPD emulsions are divided into two main types: radial and axial. The radial device is considered above (**Fig. 3.14**), and in the axial devices, the initial components move in the axial direction. Here, the processing of the medium takes place in a narrow gap between the flat discs of stators and rotors with radial slots. The efficiency of such devices is lower than that of radial devices. Radial-type RPDs provide more uniform processing of the medium and are easier to manufacture and operate.

The spectrum of RPD designs, their technological characteristics, and the structure of unsteady flows of processed products are given in works [18]. The peculiarity

of unsteady flows in RPD is the variety of their forms (cavitation, non-cavitation, resonant, non-resonant, oscillating, and others), and when designing to maximize cavitation, numerous methods of its excitation are added (acoustic, hydrodynamic, mixed, pulse, resonant, high-frequency, low-frequency, etc.).

RPDs make it possible to intensify technological processes due to carrying them out in non-stationary conditions, using the energy of sound vibrations and secondary acoustic effects, due to the discrete introduction of energy into the processed medium. The devices that most fully meet all of the above requirements include rotary devices with different names:

– rotor apparatus with flow modulation (RAFM);
– rotary-pulsating device (RPD);
– rotor-type pulsating device (RTPD);
– rotor-type hydrodynamic apparatus (RTHDA);
– liquid, hydroacoustic sirens, "Ultraturrax";
– hydromechanical disperser.

These devices are distinguished by their simple design, high reliability and efficiency. They have the same basic design scheme, but the mechanism of action on the processed emulsion of these devices is significantly different, which is related to the size of the radial gap between the rotor and the stator. In rotary devices such as RAFM, RTPD, hydromechanical dispersers, the gap is sought to be minimal – no more than 0.1 mm, while in RPD the indicated gap is more than 0.2 mm and can reach several millimeters. Intensification of dispersion processes in rotorcraft is primarily facilitated by intense pulsed acoustic cavitation [18], high turbulence and a high velocity gradient in working volumes [19].

Most RPD is designed to create advanced cavitation.

Rotary devices are distinguished by the simplicity of their manufacture. Their energy efficiency is due to the fact that the liquid medium is both a source and an object of oscillations and, thus, the mechanical energy of the processed liquid medium is directly transformed into useful energy – necessary for dispersion. Impulse concentration of energy in short periods of time determines their high intensity [19]. The time and frequency of exposure to the emulsion can be adjusted by feeding the product into the RPD.

When studying the dispersion of emulsions processed in RPD, it was established that, in general, the average diameter of the particles of the dispersed phase does not exceed 1 μm [9], but the dispersed composition is uneven and contains an increased number of undisrupted fat globules.

To describe the mechanism of dispersion of emulsions in RPD, three main hypotheses are used: cavitation, turbulence, and gradient. A high velocity gradient ($6.8 \cdot 10^6$ s^{-1})

is created in the gap between the rotor and the stator, which can be compared only with the velocity gradient in the working gap of the valve homogenizer ($8.4 \cdot 10^6$ s^{-1}) [9]. At the same time, high values of the velocity gradient almost uniformly cover the entire volume of the working gap, in contrast to the valve homogenizer. In addition, in the RPD, compared to the valve homogenizer, the time of action of disruption factors increases. But these advantages of RPD did not allow obtaining a dispersion degree comparable to a valve homogenizer. Therefore, the hypothesis of gradient disruption was not experimentally confirmed.

In the 1980s, the prevailing hypothesis of homogenization in RPD was turbulent dispersion. But the authors failed to find experimental confirmation of this theory by visual observation data. In recent times, most RPD researchers use the hypothesis of cavitation disruption as a basic one.

Pulsating devices with a vibrating rotor. A variety of rotor-pulsating devices is a design with a rotor that performs axial oscillations (vibrations) during operation – a pulsating device with a vibrating rotor (PD with VR) [20]. When additional oscillations are imposed due to the vibrating rotor, the energy distribution becomes uniform, and due to the coordination of the rotor oscillations with the overlap of the holes, a resonance of pulsations is created, which additionally increases the efficiency of the process in comparison with the classical RPD. This leads to an increase in the uniformity of the dispersed composition of milk after homogenization and a decrease in the energy consumption of the process. But studies of the operation of such a device were practically not carried out.

Centrifugal rotor homogenizers. In centrifugal homogenizers, under the influence of the rotation of the rotor, liquid under pressure passes through nozzles or slotted holes and hits special reflectors. The disruption of fat globules occurs due to cavitation in cavitation cavities, which are formed behind reflectors [21].

Centrifugal devices are simpler than valve devices, they are less metal-intensive, they do not have fast-wearing plunger pairs. Their main drawback is a low degree of milk homogenization (the average size of fat globules is more than 2 μm) and significant foaming of the product during its processing. Such devices are more often used as mixers, and not as homogenizers.

Colloid mills. Fine dispersion can be carried out in fine grinding mills when the product passes through thin gaps between the working bodies of these machines [22]. But in order to create an emulsion with a dispersion of 1 μm, it is necessary to create developed friction of the working organs of the mill, which contaminates the emulsion with wear products of the surfaces of the working organs and significantly increases the required power of the process. Therefore, colloid mills were not used for milk homogenization.

Vacuum homogenizers. During vacuum homogenization, in addition to dispersing milk fat, such additional advantages are achieved as: reducing acidity, increasing heat resistance, degassing, deodorizing milk, as well as partial inhibition of microflora [23]. The essence of the method is based on the fact that two- or three-fold adiabatic sudden boiling of milk in the chambers leads to crushing of milk fat globules.

In the developed VG-5 vacuum homogenizers, the size distribution of fat globules is comparable to processing in valve devices, but their average size is significantly larger and is 1.5–2.5 μm. The mechanism of milk fat dispersion in vacuum homogenizers differs significantly from other devices in the absence of cavitation. Despite this, when milk drops are boiled in a vacuum chamber, the fat globule enters conditions similar to the hydrodynamic conditions in the zone of high local pressures around the collapsing bubble. That is, intense local pressures act on the fat globule, causing microvortices, which, according to the turbulent theory of disruption, are the cause of the disruption of milk fat globules.

Cavitation devices for dispersion. The principle of operation of cavitation dispersers is based on the use of oscillations from vibration (tens and hundreds of Hz) to the acoustic ultrasonic range (>103 Hz) for the disruption of dispersed phase droplets [24]. Hydromechanical and hydrodynamic generators are used to create oscillations.

According to the principle of operation and construction, cavitation devices are divided into 4 types:

– hydrodynamic (cavitation is generated hydrodynamically as a result of choosing the shape of the working chamber, or by placing cavitating elements in the latter – cavitators);

– hydroacoustic (with and without a resonator) – in which cavitation occurs as a result of pressure pulsations from the vibrations of the acoustic emitter in the ultrasonic frequency spectrum;

– vibrating, in which cavitation occurs as a result of variable pressure due to vibrations caused by external stimuli, such as piezoelectric, magnetostrictive and electrodynamic;

– discharge-impulse, in which a high-voltage discharge in a liquid (electrohydraulic effect) is used, as a result of which electric breakdown in the area surrounding the discharge channel creates high pulse pressures, shock waves and acoustic cavitation.

The intensifying effect of hydrodynamic cavitation is due to the occurrence of a number of effects, namely: pressure pulsations (10^2–10^3 MPa) and rarefaction-compression waves during the pulsation of steam-gas cavitation bubbles; cumulative microcurrents of high energy potential, which destroy phase interfaces; phase transitions on the surface of the bubbles; temperature pulsations (over 10^3 K) due to the collapse of cavitation bubbles.

Cavitation devices are much less energy-intensive than valve devices, compact and easy to maintain, while simultaneously with dispersion and emulsification, the disruption of microflora and cells of microorganisms. Acoustic emulsification makes it possible to obtain dispersion of emulsions starting with a size of 1.2–1.8 μm, which is significantly greater than dispersion after processing in valve homogenizers.

Electrohydraulic homogenizers. Due to extremely high-pressure pulses in the processed product, shock waves are created, which lead to the effect of electro-hydraulic shock. This creates high local pressure and velocity gradients and cavitation, which leads to the dispersion of fat globules to sizes less than 1 μm. But for the uniformity of emulsion processing, it is necessary to significantly increase the processing frequency, which reduces the energy efficiency of the device and worsens the dispersion composition of the emulsion, due to the simultaneous coalescence of fat globules. The taste of the product changes with long-term action of electrohydraulic influence.

Jet and stream homogenizers. In jet (stream) devices for dispersing the fat phase of milk, homogenization occurs due to the action of a jet (both free and submerged) or a product flow.

The jet homogenizer is a nozzle or nozzle, the jet of which:

– reflected by a closely located reflector (drums);

– immersed in the dispersion liquid of this emulsion (separate homogenization) [25];

– collides with another jet (counter jet) [13];

– exits into a larger chamber, due to which cavitation caverns are created;

– creates hydroacoustic and hydrodynamic cavitation both due to the cavitator, resonator, and due to alternating high and low pressure (cavitation) zones.

OGV nozzle homogenizer was developed by V. Ya. Granovsky. The homogenizing head of this homogenizer consists of two chambers, in the first of which the product is given rotational movement, in the second – translational movement when the liquid passes through the nozzles. Homogenization occurs when the product is injected into the second chamber and when it exits the nozzle. According to the author, the vortex movement of the medium does not play a special role. The main principle of the disruption of fat globules is due to cavitation and turbulence. Therefore, the efficiency of homogenization is 80 % at a pressure of 10 MPa, and the average diameter of fat globules is 1.2 μm, which is 1.5 times larger than in a valve homogenizer.

High sliding velocities are achieved in **counter-jet homogenizers** consisting of two coaxially located nozzles. The dispersion of the fat phase of milk is very high (0.7–0.8 μm) and is comparable to the dispersion achieved in valve homogenizers. Despite low energy consumption and high processing quality, significant foaming prevents the widespread use of such devices [13].

Jet homogenizers that do not have the above-mentioned drawback are homogenizers with separate feeding of the fat phase into the jet of skimmed milk, or skimmed milk into the jet of cream (T-homogenizers) [25, 26]. Such devices make it possible to achieve a high velocity difference between the fat globule and plasma and are not inferior to valve devices in terms of homogenization efficiency. Due to the use of separate homogenization (treatment of only the fat phase), they have low energy consumption (less than 2 kWh/t) [25]. They can also combine the operation of normalizing the milk mixture by fat content, but at the same time, they require preliminary separation of milk into cream and skimmed milk (separation). Due to the need to use thin channels to increase the dispersion degree, counter-jet devices have a high tendency to obliterate the inner surfaces of the nozzles (overgrowth with a product layer). Also, this type of homogenizer makes high demands on the purity of the cream to prevent channel clogging.

Hydrodynamic and hydroacoustic cavitation devices are structures in which cavitation is initiated by alternating zones with different velocities or by interaction of a jet (flow) with a cavitator or resonator. The advantages of hydrodynamic cavitation (decrease of pressure in the flow to values close to the pressure values of saturated water vapor under appropriate conditions) compared to acoustic cavitation are the uniformity of spatial processing of the liquid phase medium and high productivity.

Microfluidizers make it possible to obtain the highest dispersion degree with the sizes of dispersed particles smaller than in the valve UHP homogenizer: 10–100 nm and a narrower range of distribution of fat globules by fractions [27]. The microfluidizer consists of a loading tank, a high-pressure pump (from 100 to 300 MPa) and a working chamber where two (or more) emulsion jets collide at high velocity (more than 400 m/s). During the passage of flows through thin channels (50–300 μm), significant shear stresses (gradient up to 10^7 s^{-1}) arise in the liquid, and during the collision in the shock chamber, high turbulence, cavitation, and high velocities of fat globules flow around.

Microfluidizers allow multiple processing if necessary, but have high specific energy consumption and low productivity (5–50 liters per minute).

Pulsation piston homogenizers. There are devices where the emulsion is formed due to the reciprocating movement of the piston – the so-called pulsating (pulsation) devices [10]. They are usually made in the form of plates or disks with holes, fixed on vertical rods that perform reciprocating movements. The downward or upward movement of the impactor piston causes the dispersion phase to move at a velocity υ_{pl}, which flows around the fat globule moving in the opposite direction due to the inertial force F_i (**Fig. 3.8**).

There are also pulsating devices, which are structurally made in the form of a camera immersed in the device with a system of various nozzles. The dispersion

of the emulsion exceeds this indicator for valve homogenization due to the creation of high sliding velocities of the fat globule.

A pulsating homogenizer with two pistons connected by an elastic element showed high efficiency. With the dispersity of the milk emulsion at the level of valve homogenizers, the energy consumption of an industrial model is less than 2 kWh/t.

Impulse impact homogenizers. Dispersion of milk emulsion in pulse homogenizers occurs with piston disturbances with an intensity of 1.5 MPa and a frequency of 50 Hz, created with the help of hydraulic or pneumatic pulse drives [10]. In such homogenizers it is possible to obtain an emulsion with a dispersion that exceeds the parameters of valve homogenizers (0.5 μm), with energy consumption less than 4 kWh/t, which is 2 times less than valve homogenizers. The proposed hypothesis of homogenization in impulse devices (by blowing microparticles from the surface of the fat globule) is questionable due to the complexity of implementing such a disruption mechanism for milk, the density of the dispersed and dispersed phases of which differs by only 5–6 %. But this hypothesis is based on the creation of the sliding velocity according to Weber's criterion, which generally coincides with modern ideas about the homogenization mechanism. The creation of pressure pulses (disturbances) of high intensity is a consequence of the use of a drive with a high braking and acceleration effect, which requires high energy consumption.

High-velocity mixers. Stirrers with a high rotation frequency are universal and widely used equipment for creating stable emulsions of various compositions [17, 28]. They create high velocities of product movement and, unlike valve ones, unlimited time of impact of destructive forces. The variety of constructions of working bodies contributes to the possibility of creating high gradients of emulsion movement. But the mode of operation of mixers is periodic. For uniformity of dispersion during the operation of the stirrer, the product undergoes multiple processing, as a result of which one microvolume of the emulsion is subjected to many "extra" influences of the working bodies, which do not lead to the dispersion of dispersed particles, which significantly reduces the energy efficiency of the process. With constant movement of the stirring organs, despite the high velocity of the emulsion, the velocity gradient decreases, which reduces the dispersion degree. To increase it, it is necessary to use pulse modes of movement of the mixer, which are energy inefficient due to high energy consumption during acceleration and braking. Thus, high-velocity mixers have not been widely used for the preparation of microemulsions, such as homogenized milk, and are most often used as emulsifiers (with the required dispersion of more than 2 μm).

Vortex homogenizers. Vortex homogenizers are designed to create maximum dispersion conditions according to the theory of low-temperature cavitation homogenization, the driving force of which is sublimation [29]. The design of this type

of homogenizer is based on the principle of a vortex tube, the theory of which is currently not developed, which, according to the authors, allows obtaining the maximum length of ultra-low pressure zones.

The dispersity of the emulsion after processing in the vortex apparatus reaches 1.2 μm, and the energy consumption is at the level of countercurrent-current 3.8 kWh/t.

The Y9-OGZ brand jet-vortex apparatus is an emulsification block with six holes with a diameter of 5 mm. The productivity of the machine is 8,000 l/h, the working pressure is 0.3–0.4 MPa. The average diameter of fat globules after processing in an emulsor is 1.6–2.2 μm.

Let's analyze the main dispersing factors in modern homogenizers of the dairy industry (**Table 3.4**).

Table 3.4 Predominant hydrodynamic phenomena that lead to the disruption of fat globules of milk in the main types of devices for homogenization

Homogenizer type	Turbulence	Liquid flow gradient	Flow around a fat globule	Cavitation	Electro-hydraulic shock	Sublimation	Boiling in a vacuum
Valve (die, screw)	•	•	•	•			
Microfluidizer	•	•	•	•			
Impulse			•				
Pulsating			•				
Rotary-pulsating	•	•	•	•			
Ultrasound	•		•	•			
Counter-jet		•	•				
Vortex (jet-vortex)			•	•		•	
Jet with separate homogenization			•				
Colloid mills	•	•					
Mixers	•	•	•				
Electrohydraulic				•	•		
Vacuum							•
The main hydrodynamic factors of disruption	Relative velocity of dispersed and dispersive phases and emulsion flow acceleration						

Developers and researchers of homogenizers consider the main causes of dispersion to be turbulence, liquid flow gradient (in longitudinal and transverse directions), flow around a fat globule, and cavitation. Electro-hydraulic shock combines the action of cavitation and hydraulic shock (high flow gradient). But all these factors can be

combined with such hydrodynamic factors as the relative velocity of the dispersed and dispersive phases and the acceleration of the emulsion flow. Indeed, both the turbulence, the flow gradient, and the flow around the fat particle lead to the appearance of the fat globule sliding relative to the dispersion medium. This velocity is proportional to the acceleration of the liquid flow. At the same time, the acceleration factor promises to be a more universal indicator for many types of homogenizers, thanks to which it is possible to create designs of highly efficient devices with low energy consumption.

3.5 Generalization of the disruption mechanisms of milk fat globules

Although a huge number of works have been devoted to the issue of breaking up droplets (dispersion, emulsification), the first among which is the study of A. N. Kolmogorov, a sufficiently complete picture of this complex phenomenon does not exist. The most significant results related to this problem were also published in the works of V. G. Levych, R. I. Nigmatulin, H. A. Stone. In apparatuses with stirrers, research was carried out on the crushing of drops in the absence of coalescence, as well as the process of mass transfer from bubbles and drops.

Stone singled out four reasons for the internal movement of a liquid in a droplet: shear flow during a continuous medium; interphase tension; movement caused by droplet buoyancy (i.e. density difference); a change in interfacial tension (Marangoni effect) and/or the presence of surfactants.

Let's try to generalize the possible mechanisms of disrupting fat globules and evaluate the degree of their influence on the final size of particles of the dispersed phase. At the same time, let's consider systems without surface-active substances and with constant interphase tension. The number of such mechanisms reaches ten:

1. Kelvin-Helmholtz instability, arising as a result of a sufficient difference in velocities between the dispersed and dispersive phases.

2. Rayleigh-Taylor instability, which occurs when the force vector is directed from a heavy liquid to a light one (a liquid with a higher density to a lower one).

3. Disrupting droplets in a turbulent liquid flow caused by turbulent pulsations.

4. Tolmin-Schlichting instability, which occurs during the transition from a laminar mode to a turbulent one, when a parallel-jet laminar flow becomes unstable due to the dominance of inertial forces over the forces of viscous friction; can also occur in homogeneous systems.

5. Benardo instability, which occurs due to density fluctuations (when heavy layers of liquid are above light ones), caused in turn by temperature and concentration gradients; can also occur in homogeneous systems.

6. Cavitation mechanism: when a cavitation bubble collapses, due to a local drop in pressure, a stream appears on the surface of the liquid interface, followed by the detachment of one or more drops from it. According to B. G. Novytskyi, this process can also occur due to the transfer of drops of one liquid on the surface of a cavitation bubble during its migration into another liquid (flotation). There is also a hypothesis about the cumulative mechanism of cavitation emulsification.

7. Dynamic – the occurrence of internal dynamic pressure in the drop, caused by toroidal flow or even turbulent movement in it, capable of overcoming external pressure and capillary forces.

8. Crushing of drops near solid walls and other elements of the device.

9. The presence of shear and tensile stresses in a continuous medium capable of significantly deforming a droplet – Couette flow, various types of hyperbolic flows.

10. In case of non-stationary movement of liquids, another droplet crushing mechanism is possible – inertial, experimentally and numerically studied by Stone.

Let's note that most often there is no sharp boundary between the described mechanisms, sometimes some of them can be reduced to others. For example, dynamic and inertial to one degree or another can be considered equivalent.

Let's consider the role of these mechanisms in the disruption of fat globules, for which let's compare the diameters of fat globules of milk in a pulsating resonance apparatus, RPD of cylindrical and disk-cylindrical types (properties of the mediums at a temperature of 60 °C: $\rho_1 = 923$ kg/m^3, $\rho_2 = 1030$ kg/m^3, $\mu_1 = 1.8 \cdot 10^{-3}$ Pa·s, $\mu = 5 \cdot 10^{-3}$ Pa·s, $\sigma = 0.05$ N/m) [30]. RPD properties: the frequency of longitudinal oscillations of the rotor is 50 s^{-1}, the radial velocity in the apparatus is 32 m/s, the maximum velocity in the modulator of the apparatus is 130 m/s.

The analysis results of the globule disruption mechanisms are summarized in **Table 3.5** [18, 20].

Table 3.5 Results of calculating the size of milk fat globules

Dispersion mechanism	Globule disruption mechanisms									
	1	2	3	4	5	6	7	8	9	10
Pulsating resonance apparatus										
d, μm	1.2	1.67	75	–	–	3.6	0.43	8.2	3000	0.68
Cylindrical rotary-pulsating device										
d, μm	0.1–10	0.15–6	0.2–2.5	–	–	4.3	3.8	4.3	94	0.12–6.9
Disk-cylindrical rotor-pulsating apparatus										
d, μm	1–135	1–133	–	–	–	300	–	17–38	28–633	–

Having analyzed the results of the table, it can be concluded that the dominant mechanisms that give the data closest to the experimental ones are Kelvin-Helmholtz, Rayleigh-Taylor, inertial and dynamic instabilities.

In addition to the above reasons for the deformation and crushing of drops in an oscillating liquid, there may also be specific mechanisms associated with the fluctuations of the drop itself.

Rayleigh obtained an expression for calculating the natural frequencies of small oscillations of a liquid drop "near its spherical equilibrium figure":

$$f_n = \frac{1}{2\pi}\sqrt{\frac{8n(n-1)(n+2)\sigma}{[(n+1)\rho_2 + n\rho_1]d^3}}, \tag{3.1}$$

where n – number of oscillations mode; σ – interphase tension, N/m; ρ_1 – density of solid medium, kg/m^3; ρ_2 – density of liquid in a globule, kg/m^3; d – globule diameter, m.

The diameter of the particle that resonates with the oscillation frequency of the emulsion and is crushed into smaller particles:

$$d = \sqrt[3]{\frac{2n(n-1)(n+2)\sigma}{(f_n\pi)^2[(n+1)\rho_2 + n\rho_1]}}. \tag{3.2}$$

The zero mode ($n=0$) corresponds to the radial expansion-compression oscillations of the drop and is impossible for an incompressible liquid, the first mode ($n=1$) corresponds to the translational oscillations of the drop as a whole, which is also impossible for a liquid with constant interphase tension. The results of calculations according to formula (3.2) at $d=2–5$ for the considered system are presented in **Table 3.6**.

Table 3.6 The diameter of the particle that resonates with the oscillation frequency of the emulsion of the self-oscillations of the spherical droplets

f_n, Hz	Globule diameter, μm			
	2	3	4	5
10	5500	7600	9400	11000
100	1200	1600	2000	2400
1000	260	350	440	510
10000	55	76	94	110
500000	4.1	5.6	6.9	81

It follows from **Table 3.6** that a vibration frequency of about 500 kHz is required to disrupt a fat globule with a diameter of 5 μm. Such frequencies are difficult to achieve even in ultrasonic dispersing devices: hydrodynamic whistles, sirens, etc.

Analyzing the application of the above mechanisms for disrupting a fat globule of milk moving in the medium of milk plasma, let's leave in the formulas only variable factors, considering density, viscosity, surface tension and other constants as constants. The results are given in **Table 3.7**.

Table 3.7 Analysis of essential factors for disrupting a fat globule of milk

Dispersion mechanism	Character of dependence of particle diameter on main factors
Kelvin-Helmholtz instability	$d \sim \frac{1}{\upsilon^2}$
Rayleigh-Taylor instability	$d \sim \frac{1}{\sqrt{a}}$
Disrupting drops in a turbulent liquid flow (according to Kolmogorov and Levych)	$d \sim \frac{L^{2/5}}{\upsilon^{6/5}}$
The dynamic mechanism of disrupting drops (according to Levych)	$d \sim \frac{1}{\upsilon^2}$
Sliding mechanism of emulsification (according to Gopal)	$d \sim \frac{1}{\upsilon}$
The inertial mechanism of disrupting drops	$d \sim \frac{1}{\upsilon^2}$

Analyzing the data in the **Table 3.7**, it is possible to understand why most authors use the Weber's criterion to assess the dispersion degree of milk fat [12]:

$$We = \frac{\rho_2 U^2 d}{\sigma}, \text{ or } d \sim \frac{We}{U^2}. \tag{3.3}$$

According to this criterion, the diameter of the globule is inversely proportional to the square of the velocity, which coincides with most dispersal mechanisms, or is close to them. Also, with the data in the table, it is possible to explain why the authors use the velocity of the flow, where the fat globule moves, instead of the sliding velocity of the fat globule (the difference in velocity between the fat globule and the surrounding plasma). This is a simple way, but it does not reflect the essence of the phenomenon at all. The sliding velocity is extremely difficult or impossible to calculate and estimate. Indeed, the velocity of the flow can be as high

as desired, but if the fat globule moves together with the dispersion medium, then its sliding velocity is zero, and its disruption does not occur. Dispersion occurs only with a sudden change in the flow, which occurs in valve homogenizers at the moment of passing through a narrow gap and in jet homogenizers when the jets collide. At the same time, the jet change rate will be proportional to the jet rate ($\upsilon \sim U$), which is experimentally confirmed by homogenization experiments in valve and jet homogenizers [5, 7, 31].

3.6 Justification of intensification methods of the dispersing milk emulsion process

To increase the efficiency of homogenization: reducing energy consumption and/or increasing the homogenization degree of milk emulsions is used:

– separate homogenization;
– imposition of mechanical vibrations on the processed emulsion;
– resonance phenomena;
– multiple processing;
– multi-stage homogenization.

3.6.1 Use of separate homogenization

Separate homogenization involves separation of cream from milk by separation and homogenization of only the fat phase (cream) [32]. Homogenized cream is mixed with skim milk after homogenization. This form of homogenization is widely used in the production of pasteurized milk. A significant reduction in the volume of the product to be homogenized proportionally reduces energy consumption by up to 80 % and the required productivity of the machine (approximately 5 times). When processing cream in a valve homogenizer, the required homogenization pressure is reduced by 20–40 % compared to milk.

Some types of homogenizers (jet with separate feeding of the fat phase and T-homogenizers) require mandatory separation of milk before feeding it into the machine. The disadvantage of separate homogenization is the additional costs for separating milk into skimmed milk and cream. There are restrictions on the maximum fat content of cream for processing in a valve homogenizer (18–20 %). In addition, the coalescence degree of fat globules increases, which can lead to a deterioration in the quality of the homogenized emulsion.

3.6.2 Imposition of mechanical vibrations on the processed emulsion

A group of researchers [18–20, 33] studied the effect of low-frequency pulsations on the course of dispersion. The experiments showed that at relatively low frequencies (of the order of tens and hundreds of Hz) and amplitudes of the order of 10^{-3} m, phenomena similar to those occurring in the voiced with the ultrasound liquid are observed, such as vibroturbulation, development and collapse of cavitation bubbles, dispersion of drops, etc., which are of direct interest from the point of view of intensification of the milk homogenization process.

Let's compare two ways of introducing energy into a liquid: in classic homogenizers and when imposing mechanical vibrations. If to consider the power dissipation in such homogenizers as valve, pulsating, rotary, and jet homogenizers, then due to the high unevenness of its distribution over the device volume (in the wall zones of the working organs, the velocity gradient is an order of magnitude higher than in the central ones), the power dissipation does not occur on the surface phase separation, as a result of which energy is used inefficiently. There are well-known cases when, for example, no more than 10 % of particles circulate in an emulsion that is processed three times longer than others, which are "lucky" to more often fall into the zone of action of local pressure gradients and cavitation. Since the entire volume of a heterogeneous liquid vibrates when a vibration is applied, it is logical to assume that dissipation will occur in the entire volume with the same intensity. At the same time, stagnant zones with a low velocity gradient and deficiencies in the dispersed composition of the processed product will be eliminated. Thus, by directing the energy introduced into the device, mainly on the interface of phases, and also in the conditions of resonant oscillations, it is possible to achieve the maximum reduction of energy consumption.

Vibration of working bodies is successfully used in pulse, pulsating and rotary-pulsating devices with a vibrating rotor. As experimental studies show, it is in these types of homogenizers that the highest degree of milk emulsion dispersity is achieved with energy consumption 2–4 times lower than the energy consumption of valve homogenizers.

3.6.3 Use of resonance phenomena

The use of externally controlled vibrational influences to create resonance in mass-energy exchange processes is a known way to significantly intensify dispersion processes [34].

In the mechanics of linear systems without damping (conservative systems), a sharp increase in the amplitude of constant forced oscillations of the system, caused by the proximity of the frequency of external periodic influence on the system and one of the frequencies of its own (non-damping) oscillations, is called the phenomenon of resonance [20]. The peculiarity of these influences is that the frequency of oscillations of the exciting external force corresponds to the frequency of the self-oscillations of the system "apparatus – heterogeneous medium being processed" and is consistent with the maximum mass-energy transfer either in the heterogeneous medium itself or at its boundaries (for example, the walls of the apparatus). At the same time, there are advantages compared to traditional devices, which are associated with a decrease in energy consumption, an increase in relative velocity, volume fraction and a decrease in the size of particles (drops and bubbles).

The features of phase relations during resonance in systems with viscous dissipation (when the friction force is proportional to the velocity of movement) include the vector balance of inertial and elastic forces, between which the reactive component of power is exchanged, and the balance of the vectors of the external (forcing) force and the force in strong friction, and the external force performs work to compensate for losses of active power. Thus, resonance is characterized by the fact that external influences at a steady state of oscillations are needed only to maintain the amplitude of oscillations achieved during the transient process and are spent entirely on compensating for energy losses caused by dissipation in the system. For this reason, the requirement to carry out processes at resonance is taken into account by many researchers when designing pulsating devices.

The analysis of the sizes of drops and bubbles formed in resonant oscillatory apparatus showed that the dominant mechanisms of fragmentation are dynamic, due to high relative oscillating velocities of the phases or their accelerations; the role of turbulent pulsations is secondary [35].

The disadvantage of using resonant modes of operation of the equipment can be an increased mechanical load on the moving parts and units of the device.

In valve, rotary, pulsating and jet homogenizers, the consumed power is dissipated not only on the contact surface of the phases, but also in the entire volume, as a result of which the energy consumption of the device is much greater than the energy required for dispersing fat globules of milk. It is natural to expect that one part of the fat globules will not have time to collapse, and the other will have time to be exposed to destructive forces multiple times. In order to remove to a large extent of the listed drawback, it is necessary to create significant accelerations in mediums with an excellent density of phases.

Let some volume of liquid containing a particle or a globule oscillate. Due to the difference in density, relative periodic slippage of the particle will be observed. Thus, energy dissipation will occur near the phase interface, and all the power supplied to the device will be converted into useful power. Since the entire volume of the heterogeneous medium oscillates, it is logical to assume that with uniform distribution of particles throughout the device volume, dissipation will occur with the same intensity throughout the volume and the forces of interphase interaction will also be the same.

But during the improvement of devices intended for the creation of homogeneous emulsions and dispersions, the creation of conditions for the emergence of resonant vibrational or acoustic oscillations, only in rare cases attention was paid to such an issue as the correspondence of the mode parameters (frequency, amplitude, velocity) of the device to the optimal conditions for homogenization [36]. Thus, the restraining factor in the use of resonant oscillating homogenizers is insufficient study and lack of reliable methods for calculating amplitude-frequency, hydrodynamic and mass transfer characteristics, especially in the resonant mode of oscillations.

Analysis of the design of rotor-pulsating devices with intensification of the process of dispersing the dispersed phase of the emulsion by resonance phenomena. Over the past 20 years, more than 100 patent documents aimed at improving the RPD design have been suggested, and not always the given changes lead to an increase in the efficiency of the process. An analysis of the main design solutions of the RPD, which allow to increase the dispersion degree and/or reduce the specific energy consumption of this process due to resonance effects. Let's dwell in more detail on the most promising, in our opinion, RPD design, in which the rotor, in addition to rotation, performs axial oscillations of a pulsating device with a vibrating rotor. Such RPD (**Fig. 3.15**) consists of a housing 1 in which an electromagnet 10 is mounted.

The rotor 4 is mounted on the shaft 7 and pressed by the spring 8 to the nut 9. The stator 5 is rigidly fixed on the cover 6. There is a minimum gap between the rotor and the stator. The device also includes a cover 11, a seal 12, nozzles 2 for input and 3 for output of components.

The device works like this. The medium processed through the inlet pipe 2 enters the central part of the device and, under the action of centrifugal forces, passes into the gap between the rotor 4 and the stator 5. Due to the impact of the particles on the teeth of the rotor and stator, as well as shear stresses arising in the gap, the particles are being grinded. When an alternating voltage is applied to the coil of the electromagnet 10, axial oscillations of the rotor 4 occur.

The gap increases at the moment of its attraction to the electromagnet. The value of the radial gap is a variable value in time, which allows changing the value of the shear stresses of the heterogeneous medium. In the process of rotor rotation,

there is a periodic overlap of the slots, as a result of which a hydraulic shock occurs and the acoustic vibrations are generated. Thus, elastic oscillations and axial vibrations are simultaneously applied to the processed medium. For the device to work effectively, the following condition must be met: the frequency of rotor vibrations is a multiple of the overlapping frequency of the rotor slots. After passing through the active zone, the mixture enters the outer chamber and is discharged through the nozzle 3. Thus, in the suggested design of the RPD due to the electromagnet installed in the body, it is possible to process the medium in resonance conditions, which allows to intensify the technological processes in it and improve the quality of the obtained product.

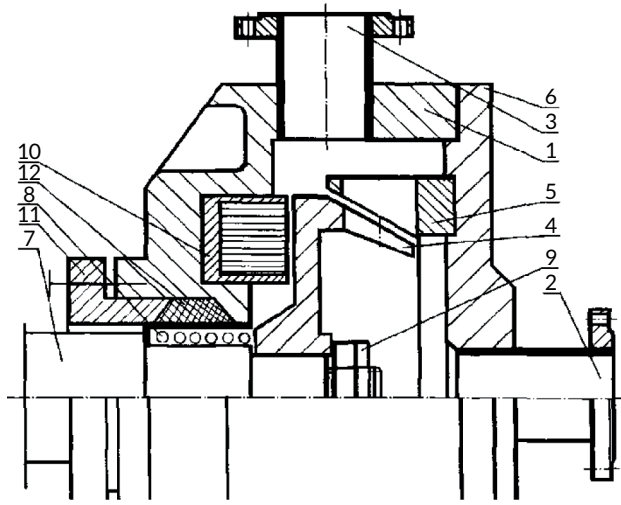

Fig. 3.15 Rotor-pulsating device with a vibrating rotor

Based on the considered structural and technological features of the RPD, the following conclusions can be drawn [37, 38]:

– almost all structural elements are designed to increase the amplitude of pressure pulsations, shear stresses, the development of turbulence and/or cavitation;

– in the existing designs of resonators in the form of needles, membranes and other elastic elements, it is impossible to create modes where the frequency of vibrations and pulsations can be adjusted independently of the rotor rotation frequency. Such possibilities are present only in structures where the rotor oscillates relative to the axis of rotation, which can be controlled independently of the rotation of the rotor;

– for PD with VR, it is noted that the rotor vibration frequency must be a multiple of the overlapping frequency of the holes, which creates conditions for the occurrence of resonance;

– studies of dispersion quality and thorough theoretical studies of RPD with mechanical vibration generators have not been carried out, therefore, the study of such devices is a promising direction of further research, which can increase the efficiency of emulsion homogenization in RPD.

3.6.4 Multi-stage homogenization

Multi-stage homogenization has been established in valve homogenizers. For this purpose, the valve head consists of two independent "valve-seat" sets. The milk successively undergoes the first stage of processing (under pressure through the annular gap formed by the valve and saddle), and then through the second. The main advantage of multi-stage homogenization is a reduction in the size of fat globules and a narrower distribution of their sizes.

The pressure of the second stage (P_2) is lower than the pressure of the first stage (P_1). The best results are obtained when using the pressure of the second stage of $0.2P_1$. The second stage creates a decrease in the pressure drop on the first stage of the valve homogenizer [39]. The mechanism of influence is explained by: changes in the cavitation mode in the valve gap of both stages, changes in turbulence or the disruption of agglomerates of fat globules that formed after passing through the first stage of the valve head.

Two-stage valve homogenizer heads are serially produced, which allow reducing the specific energy consumption of the process by 15–20 % [7]. At the same time, the pressure at the second stage of homogenization is lower than the pressure at the first stage. In addition to valve homogenizers, two-stage homogenization is used in vacuum homogenizers of the GV type.

The mechanism of energy consumption reduction during multi-stage homogenization is explained: firstly, by increasing the exposure time of the hydrodynamic factors of disruption, and secondly, by covering most of the fat globules with its destructive factors.

3.6.5 Multiple processing

Increasing the multiplicity of fat emulsion processing – the number of passes through the working bodies of the homogenizer – is used in many types of

homogenizers, such as ultrasonic, pulsating, die, jet, electrohydraulic, and mixers. Multiple passing of the product through the working organs of the device leads to a significant increase in emulsion dispersion (by 2 or more times), in contrast to two-stage homogenization, due to which dispersity increases by a maximum of 20 %.

For mixers, ultrasonic and electro-hydraulic devices, multiple processing is necessary to achieve high dispersion due to the fact that the working bodies in one cycle of passing the emulsion do not provide either complete coverage of the entire volume of the emulsion, or the necessary intensity of impact. Involvement of most of the fat globules under the influence of destructive factors during multiple processing is necessary due to the heterogeneous structure of the flow in the homogenizers. For example, in mixers, the hydrodynamic conditions of the wall layer of the emulsion differ significantly from similar conditions in the central zone, where the flow rate is lower. The velocity gradient in the wall zones is 2–3 times higher than in the central part of the flow [15].

In contrast to the multi-stage homogenization, the hydrodynamic conditions in the working bodies do not change during multiple homogenization.

With multiple processing, the fat particles, which during the first passage through the valve gap got into zones unfavorable for disruption, can avoid such zones during the second (or more) passing. Thus, with an increase in the frequency of processing, the probability of fat globules entering the zones of the working bodies of homogenizers with hydrodynamic conditions sufficient for disruption (high velocity gradient, zones of cavitation micro- and macro-perturbations, zones of high flow acceleration, etc.) increases.

According to experimental data obtained by E. V. Nuzhin [7] for valve homogenization, the dependence of homogenization efficiency on multiplicity (the number of passes through the valve gap of the homogenizing head) is parabolic (**Fig. 3.16**).

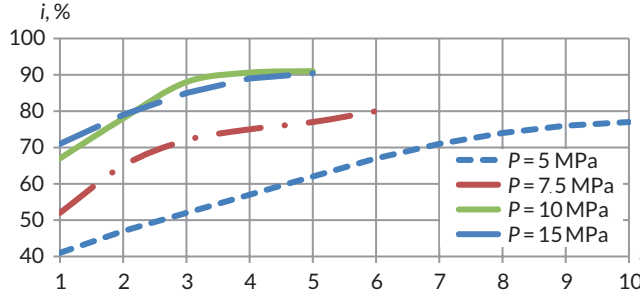

Fig. 3.16 Dependence of the homogenization efficiency (*i*) % on the homogenization pressure (*P*) MPa and the frequency of passing through the valve head *K*

Several conclusions were drawn from these data:

– when developing or improving homogenizers in order to reduce specific energy consumption, it is necessary to try reducing the frequency of passing the product through the working organs of the machine;

– it is possible to reduce the specific energy consumption of the homogenization process due to multiple processing, if at the second (or more) stage, modes with lower energy consumption are used, for example, to reduce the homogenization pressure;

– to reduce the frequency of processing, it is necessary to create the most uniform conditions of hydrodynamic dispersion in the working bodies of homogenizers;

– pressure (and homogenization efficiency) can be represented as a dependence on the acceleration of the emulsion flow in the valve gap.

Conclusions

1. Despite the widespread use of the homogenization process in the dairy industry, there is a lack of standards and regulations that regulate this process. On the basis of literature sources and technological documentation, which regulate the required pressure of the most common valve homogenizers, the dispersity of the milk emulsion, sufficient for existing dairy production technologies, has been determined: 0.75–0.85 μm.

2. It has been determined that due to the complexity of the structure of the fat globule and its shell, the generally accepted approach of considering only the surface tension as the main characteristic of the strength of the fat globule shells is erroneous.

3. A significant number of generally accepted hypotheses and theories of homogenization, which contradict each other, have been noted. The latest scientific data on the process of dispersing the fat phase in valve homogenizers confirm the validity of the turbulent viscosity theory, according to which disruption occurs as a result of Kelvin-Helmholtz and Rayleigh-Taylor destabilization. Common to these mechanisms is the creation of hydrodynamic conditions in the disruption zone, which contribute to an increase in the relative velocity of movement of the dispersed and dispersive phases and acceleration of the emulsion flow.

4. As a result of the generalization of the ideas of the milk emulsion dispersion process of the developers and researchers of homogenizers, the predominant hydrodynamic phenomena that lead to the disruption of fat globules have been established: turbulence, liquid flow gradient (in longitudinal and transverse directions), flow around the fat globule and cavitation. It has been substantiated that the mentioned

phenomena can be combined by such hydrodynamic factors as the relative velocity of the dispersed and dispersive phases and the acceleration of the emulsion flow.

5. The analysis of intensification methods of the dispersing milk emulsion process makes it possible to identify promising directions for increasing the energy efficiency of homogenizers: increasing the acceleration of the emulsion flow when using sign-changing pulsations, imposing mechanical oscillations, creating conditions for the occurrence of resonance phenomena, and optimizing the multiplicity of emulsion processing and the relative velocity of emulsion phases when implementing the method supplying the fat phase of the milk emulsion into the flow of skimmed milk. 3 principle schemes of promising dispersers have been justified to reveal the potential of the selected areas of efficiency improvement: a pulsating device with a vibrating rotor, a jet homogenizer with a separate feed of the fat phase, and a pulsating piston homogenizer.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 4

Qualimetric assessment and features of quality formation for cultivated mushrooms in accordance with the methods of further processing

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Tetiana Krupodorova

Abstract

Recently mushrooms, due to their special functional properties, are confidently included in the daily diet of people who consider the possibilities of nutrition to improve their health. Therefore, the production and consumption of mushrooms, as well as products of their processing, is growing rapidly, and the range of species available on the market is actively expanding. In this study, the topical issues of expanding the assortment and quality of cultivated mushrooms are highlighted, the main principles of ensuring the quality of the mushroom harvest are considered. The possibility of preserving the value of the harvest by expanding the options for processing mushrooms is also examined. The difficulties and visible prospects of expanding the range of products are considered. The monograph discusses the factors that determine the quality of the harvest of cultivated fungi of the genera *Calocybe*, *Cyclocybe*, *Pleurotus*, and the features of the qualitative assessment of mushroom raw materials in accordance with the directions of its processing. The parameters for a comprehensive assessment of qualitative indicators of fruiting bodies of *Calocybe indica*, *Cyclocybe aegerita*, *Pleurotus citrinopileatus*, *P. pulmonarius* have been established, and the coefficients of the values of individual and group indicators of crop quality have been determined. An experimental evaluation of changes in morphological parameters in the technical and biological maturity of the fruit bodies of mushrooms was carried out, and their nutritional value has been investigated. Modern methods of optimizing post-harvest procedures and storage of mushrooms determined their critical storage terms according to directions of processing. The proposed seasonal approach to the cultivation of the studied strains indicates the possibility of reducing the cost of the mushroom crop. The qualimetric assessment of the post-harvest characteristics of strains from the domestic collection makes suggests high prospects for use the studied mushrooms for visual attraction customers to expand the range of mushroom products

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on supermarket shelves. A comprehensive analysis of the proposed qualimetric assessment and the quality features of the cultivated mushrooms studied, depending on the methods of further processing, indicates the prospects of this area of research and the feasibility of bringing other species of exotic cultivated mushrooms to the market.

Keywords

Calocybe, *Cyclocybe*, *Pleurotus*, pioppino, gold oyster mushroom, lung oyster mushroom, milky mushroom, storage, processing, quality, cultivation, market.

4.1 Introduction

Mushroom consumption properties are heavily influenced by cultural and traditional habits, and even some myths. One of the scares is the fear of toxic compounds in mushrooms with bright color caps. Another myth with deep roots is the difficulty in converting mushrooms by the digestive system of young or old organisms. Furthermore, common cuisines in some European countries have a very limited number of recipes that include mushroom ingredients. At the same time, the rapidly developing cultivation of mushrooms makes it possible to expand the range of species with proven health properties and saturate the market with a variety of mushroom flavors and textures. Therefore, the organization of an open and understandable quality management system to produce fresh mushrooms and their processed products is a topical topic. Let's believe that only the continuous improvement of this system at each stage of the production cycle and the demonstration of the results obtained to the modern consumer will help to get rid of the existing prejudices regarding the introduction of mushrooms into the daily diet of people of any age.

4.2 Actual issues of expanding the assortment and forming quality of the cultivated mushrooms

On the global mushroom market, a significant increase in demand for mushrooms is observed every year. In 2022, mushroom production was ranked sixth in the list of the total value of vegetable production. According to the Global Market forecast: "Revenue in the Root Vegetables & Mushrooms market will reach 118.10 billion USD in 2024. The average volume per person in the root vegetables and mushrooms sector is expected to reach 8.9 kg market in 2024" [1].

The observed progress is due to the unique functional properties of mushrooms, which include a high protein and dietary fiber content, as well as a low-fat content.

Such a nutrient balance fully corresponds to modern trends in healthy eating and cannot but attract representatives of the food industry. In addition, the physiological features of mushroom nutrition make it possible to regulate the nutrient composition of the crop and contribute to the accumulation of essential elements in the fruiting bodies by modelling the composition of substrates and aqueous solutions used for moistening plant raw materials and technological irrigation. It should be noted that the mushroom industry is quickly responds to market needs. Ten years ago, no more than 4 types of mushrooms could be found on the shelves of vegetable stores in European countries and North America: bottom mushroom, shiitake, oyster mushroom and eryngii. Nowadays, the range offered has expanded significantly, mainly thanks to the technical solutions of Chinese researchers who have introduced, according to various sources, from 20 to 60 species of mushrooms into commercial cultivation over the past decade [2]. If desired, a modern European consumer can diversify their daily diet with fresh exotic fungi: enoki (winter mushroom), pioppino (poplar mushroom), shimeji (beech mushroom), oyster mushrooms (lung, golden, pink) and many other species. However, the high price of fresh mushrooms and short shelf life limit the use of their health-promoting potential in the daily diet of the average consumer. Modern research in practical mycology is still focused on finding ways to expand the range of edible fungi with proven biological value and the possibility of reducing harvesting costs.

4.2.1 The basic principles of ensuring the quality of mushroom crop

The expansion of the range of artificially grown mushrooms on the world market creates additional questions regarding the determination of the quality indicators of the obtained harvest. The main indicator of quality is the food safety of mushroom products, which is clearly regulated by the requirements of Codex Alimentarius. There are three standards that control the safety of fungi and their products: CXS 38-1981 – Standard for Edible Fungi and Fungus Products; CXS 39-1981 – Standard for Dried Edible Fungi and Separate Regional Standard for Wild Chanterelles; CXS 40R-1981 – Regional Standard for Chanterelles [3]. Due to the rapid expansion of the market range, the general standardization system cannot manage all requirements to quality of edible mushrooms. To develop a quality management system for the cultivation and processing of edible and medicinal mushrooms, it is significant important to identify safety issues. The analysis of published scientific data and practical studies made it possible to the develop a program that outlines the basic principles of mushroom harvest quality (**Fig. 4.1**).

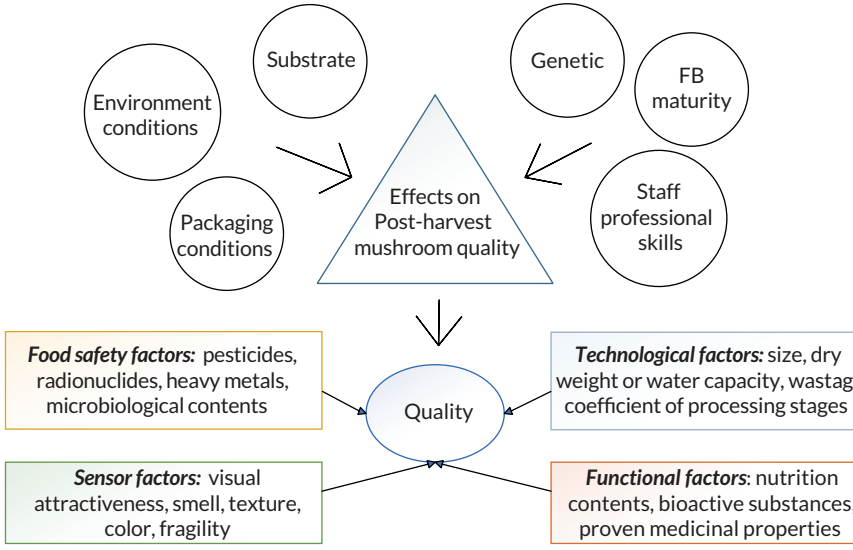


Fig. 4.1 Program of mushroom crop quality formation

According to most operators of the mushroom business, the quality of the substrates used is one of the main factors affecting the crop quality. The formula's balance of organic and mineral components, microbiological electivity, purity, and availability of raw materials are the most common factors that influence it [4, 5]. The conditions for growing mushrooms are equally important. The optimal environmental parameters for each culture are different, including temperature, humidity, lighting, and air composition [6]. The technical regulation of microclimatic conditions at each stage of mushroom culture development, considering their specific needs, is constantly being studied and improved. The shelf life of harvested mushrooms is limited. The loss of crop weight in the first hours after harvest is caused by the peculiarities of physiological processes (intensive respiration) and high enzymatic activity in fungal cells, regardless of temperature. In addition, scientists have emphasized that fruiting bodies undergo rapid changes in chemical composition and physical and microbiological deterioration during stored [7]. Clearly organization of post-harvest procedures is no less important for preserving the quality of the harvest. The organoleptic, technical, and functional properties of mushroom yield directly depend on the genetic characteristics of the cultivated species and strain. It is necessary to determine the specific time of harvesting when the appearance and biochemical composition of the fruiting bodies will meet the requirements of

the buyer or processor as much as possible. Only highly qualified personnel can implement this approach. The organization of timely analyses can be simplified through close cooperation between manufacturing companies, research centers, universities, or private laboratories.

The complexity of the qualitative assessment of the harvest lies in the need to determine the main quality indicators of mushroom products, which, first of all, must meet the requirements of the average consumer. In most cases, organoleptic characteristics are the most important elements of the evaluation. However, the formation of the pricing policy, and, consequently, the availability of mushrooms for buyers, depends primarily on the technical features of growing a particular species. As a result of the analysis of production processes at domestic and foreign enterprises for the cultivation and processing of mushrooms, ways to managing the quality of the harvest of new introduced species have been determined. Thus, following the general principle of forming complex indicators of product quality, the relative quality coefficient of a new type of crop can be determined by the formula:

$$Q_i = \frac{P_i}{P_{iSt}} (i = 1...n),$$

where P_i – value of the i-th indicator of mushroom crop; P_{iSt} – value of the i-th indicator of control (base) cultivar, for example: *A. bisporus*; n – number of indicators. It can be: P_1 – morphology or other organoleptic indicators; P_2 – dry matter (or water content); P_3 – biomass texture (dense, fibrous, delicate); P_4 – quantity of bioactive substances; P_5 – biological efficacy; P_6 – duration of the technological cycle; P_7 – terms of shelf life; P_8 – weight loss coefficients in post-harvest procedures; P_9 – market pricing policy; $P_{10...n}$ – other individual parameters.

The calculated coefficient determines the advantages (more than 1) or disadvantages (less than 1) of the implemented technology in comparison with the one already used at the enterprise. It makes it possible to consider the market reaction to a new species of mushroom, as well as the increase or decrease in production costs. The proposed formula makes it possible to analyze the features of the formation of crop quality at individual enterprises, namely:

– reasonable selection of species and strains that are of interest to the local market;

– improvement of technological solutions for the organization of microclimatic conditions;

– determination of the timing of harvesting and ways of selling the obtained mushrooms.

Local markets have specific requirements for the quality of mushrooms, which are determined by the country's consumer culture and purchasing power levels.

An individual approach is also applied to the search for technological solutions in the creation of a microclimate in the premises where mushrooms are cultivated. However, maintaining the crop quality by optimizing post-harvest procedures and processing methods are quite general that it is possible to consider in more detail.

4.2.2 Expansion of processing areas as a tool to preserve the crop value

One of the main problems of the mushroom industry is the preservation of the quality of the harvested crop, so the fruiting bodies have a short shelf life in fresh form from 2–3 days (*Hericium erinaceus* (Bull.) Pers) to a month (*Lentinula edodes* (Berk.) Pegler) [8]. Therefore, the possibilities of preserving the nutritional and biological value of mushroom crops are actively being studied. Scientists are testing improvements in post-harvest procedures post-harvesting procedures: UF lightening, modified packaging, spraying with antibacterial solution etc. One of the main ways is rapid processing into a variety of food products available to a wide range of consumers. A wide range of mushroom products, from bakery products to beverages, are already available on store shelves. Based on the results of the analysis of scientific publications containing information on the use of mushrooms in the food industry, a scheme of existing and possible processing options was drawn up (**Fig. 4.2**).

Researchers offer several options for the temperature effect on raw materials:

1) high-temperature – frying, boiling, drying;
2) low-temperature – freezing.

Baking mushrooms involves the additional use of fats, which contradicts to the general concept of a healthy eating. But today, it is a widely used approach to quick cooking of both main dishes and side dishes, as well as salads, sauces, pates. The method of frying and stewing is more often used for processing mushrooms at home and in public catering establishments: restaurants, cafes, common culinary. A separate direction of frying is the production of mushroom chips. Modern vacuum deep-frying technology can significantly reduce the fat content of such a product, making it very popular among consumers of all ages. Proponents of this processing direction are considering the possibility of balancing the nutrient composition of mushroom raw materials by introducing a fat component and making it a full-fledged component of the daily diet. The researchers emphasize the possibility of a significant reduction in microbiological objects on the surface of chips, which contributes to an increase in shelf life [9, 10]. The growing popularity of Asian cuisine has contributed to the active study of the most common method of heat treatment of mushrooms: boiling in water and steaming.

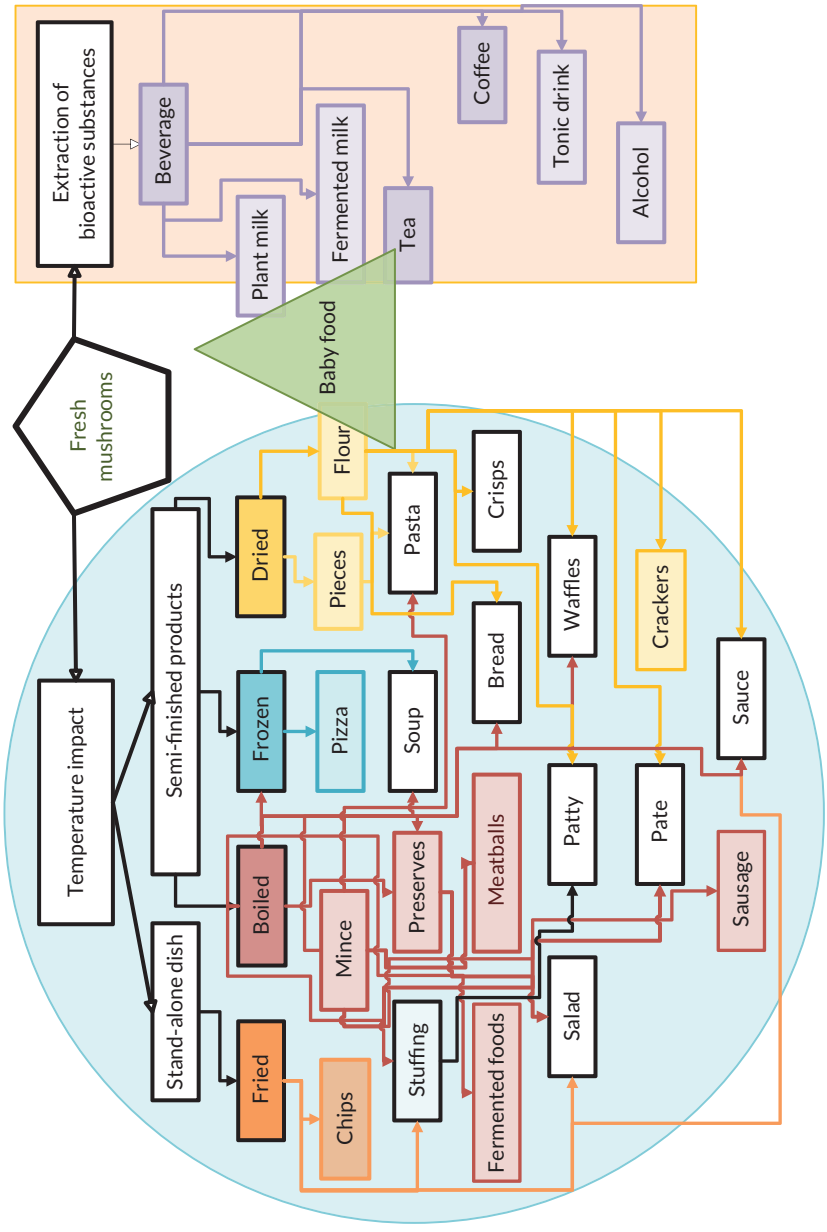


Fig. 4.2 Ways of fresh mushroom processing

Emphasizing the need to find individual solutions, the scientists argue that in order to preserve antioxidant properties, the preferred steam treatment time for *F. velutipes* was 1.5 minutes, while for *P. ostreatus* and *L. edodes* (4.5 minutes). For *A. bisporus* using a microwave oven for 1.5 minutes turned out to be the most optimal. The antioxidant value of *the P. eryngii* culture was highest in the experiment when using pressure-cooked in 100 mL of distilled water at 121 °C under 2 MPa for 15 min [11]. Blanching or short-term boiling is considered a prerequisite to produce semi-finished products, fermented mushroom products and marinades (pickles). Biological preservation of mushroom fruiting bodies using lactic acid fermentation is currently not applicable on an industrial scale; nonetheless, in the middle of the last century this method was very popular. Current research from Poland has shown the fungal raw material can be successfully preserved via lactic acid fermentation and the finished product can be an alternative to salted, marinated, or sterilized mushrooms [12]. Such products can be both independent dishes and semi-finished products, which are used in the preparation of minced meat for meat products and vegetable mixtures, fillings for pies, pate, soups, bakery products, salads, etc. Boiled or steamed mushrooms can be left whole or crushed for subsequent freezing, which allows to increase the shelf life up to 6 months [7].

Scientists do not recommend freezing mushrooms without pre-blanching or short-term boiling. Ice crystals destroy the delicate cells of the fungal tissue, which leads to a significant loss of mass and functional substances after defrosting. The deactivation of enzymes during heat treatment helps to preserve the biological value of mushrooms even during long-term storage of frozen semi-finished products (up to 12 months) [13]. For short-term storage, it is proposed to wash chopped fresh mushrooms in water containing sodium metabisulfite (5 g/l), which prevents browning of the fruiting bodies [14]. Blanched, sterilized mushrooms successfully replace frozen ones in further culinary use (soups, vegetable mixes, pies).

Drying mushrooms is considered to be the cheapest way to preserve their nutritional and biological value. Many drying methods have been studied, but the most popular is convection at temperatures up to 50 °C, as it reduces the browning of fruiting bodies and preserves their structure [15]. The proposed modern approach, which combines microwave and vacuum effects, is more expensive, but, according to the developers, makes it possible to improve the technical characteristics of the resulting semi-finished product for further use. Microwave vacuum drying made it possible to preserve a greater amount of flavor-active amino acids, as well as improve nutrient retention and color characteristics. In addition, the uniform honeycomb mesh created by microwave vacuum drying as well as the less coagulated structure of dried samples can be used to explain the observed the high rehydration factor

observed during drying [16]. The use of dried mushrooms and mushroom powders attracts the greatest attention of researchers, since the terms and conditions of storage of such semi-finished products are the most interesting for further processing. The concentration of bioactive components in dried mushrooms is much higher and is constant for a long time, which increases the possibility of regulated fortification of products for daily consumption: bakery, pasta and meat products, sauces and many other products [17, 18]. But scientists are especially attracted by the possibility of using mushroom powders to increase the health functions of baby food [19]. It has long been known about the immune-regulating and restorative effect of mushroom consumption, which is especially important in childhood and adolescence [20]. But it is also known about the low digestibility and difficulty of digestion of mushrooms in the human body. Therefore, there is a strong opinion that mushrooms and mushroom products are not recommended for those who have digestive problems and children under 12 years of age [21]. Research results confirm the safety and expediency of introducing mushroom components with a high degree of grinding or decoctions (extracts) into children's diets [22–25].

The use of aqueous and chemical extraction is one of the most used methods for obtaining bioactive ingredients of mushroom raw materials for the food industry and medicine [26, 27]. Besides conventional extraction methods, a wide range of advanced extraction technologies is available nowadays for the recovery of these bioactive ingredients from mushrooms, such as ultrasonic-assisted extraction, microwave-assisted extraction, enzyme-assisted extraction, ultrasonic-microwave synergistic extraction, subcritical water extraction, pulsed electric field-assisted extraction, aqueous two-phase extraction, integrated extraction techniques, and other novel extraction technologies [28]. Extracted fractions of mono-, oligo- and polysaccharides of mushrooms and other biologically valuable products: unique organic acids, enzymes and vitamins are successfully used in the production of various beverages [29, 30]. Unlike solid semi-finished products obtained from mushroom raw materials, extracts are easily absorbed by the human body and can be used in diets for consumers of all ages. Extracts from fruiting bodies, spore material and mycelium biomass are successfully used in the food industry.

4.2.3 Difficulties and prospects of expanding the assortment of mushroom products

Growing a variety of mushrooms is a challenging task for a farmer. As already mentioned, each species has its own characteristics that must be taken into account

when planning technological operations aimed at achieving high-quality harvest. The specific characteristics of the carpophores, which are manifested in the variety of shapes and colors of fruiting bodies, form the buyer's interest in the first place. But no less important factor for making a purchase is the affordability of mushrooms. Therefore, it is not enough to improve the visual representation of the crop on store shelves; for its successful sale, it is necessary to minimize production costs. Let's believe that one of the ways to solve such a complex issue is to cultivation of seasonal species and strains, for which the creation of optimal temperature conditions for fruiting will be the least expensive. In previous studies, 2 groups of oyster mushroom strains and pulmonary oyster mushrooms were studied, the seasonal cultivation of which made it possible to reduce the duration of technological cycles with the achievement of high biological efficiency [31]. This study examines the technological features of growing and processing four varieties of edible mushrooms in order to improve the color presentation of mushroom products on store shelves: *Calocybe indica* 2598, *Cyclocybe aegerita* 2231, *Pleurotus citrinopileatus* 2161, *P. pulmonarius* 2314. Technological regimes of growing of these strains and their impact on the biological efficiency of crops have been studied in previous studies (**Table 4.1**).

Table 4.1 Technical cultivation parameters (minimum and maximum index) according to publication data and different treatment in our previous research

Species	Days of incubation term	Days to mushroom flush	Biological efficiency, %	Fruiting temperature, °C	References
Agaricus bisporus (J.E. Lange) Imbach	13…20	18…21	49…81	14…19	[32]
Calocybe indica Purkay. & A. Chandra	19…25	4…8	90…180	25…35	[33]
Cyclocybe aegerita (V. Brig.) Vizzini	25…32	4…10	10…25	12…18	[34]
Pleurotus citrinopileatus Singer	18…30	5…8	53…85	14…28	[35]
Pleurotus ostreatus (Jacq.) P. Kumm	12…25	4…8	30…97	8…28	[36]
Pleurotus pulmonarius (Fr.) Quél	11…15	2…5	52…96	16…28	[37]

In comparison with the main cultivars of the European region: bottom and oyster mushroom (*A. bisporus* and *P. ostreatus*), it was found that the qualimetric assessment of habit and texture of fruiting bodies in the studied strains was higher. The duration of the vegetative growing period in the presented species did not exceed, and for *P. pulmonarius* 2314 it was significantly shorter than the average indicators of other species. The highest biological efficacy was recorded in the case of *C. indica* 2598

cultivation, the lowest for *C. aegerita* 2231, although in data published by other researchers these indices are higher or at the level of the main cultivars (**Table 4.1**). A significant advantage of the studied strains is the reduction of costs for maintaining the microclimate. The bright fruiting bodies of *C. aegerita* and *P. citrinopileatus* can be obtained at a temperature of 12...16 °C, and in the hot summertime produce *P. pulmonarius* and tropical mushroom *C. indica*, capable of bearing fruit at a temperature of 28 °C. It is logical that the introduction of new, species unfamiliar to the buyer will require initial marketing efforts, and the volume of their sales in fresh form is likely to be significantly lower than those of bottom or oyster mushrooms. Accordingly, the problem of maintaining the quality of the crop and finding ways to process new cultivars in a timely manner is quite acute. Therefore, the purpose of the experimental study was to conduct a qualimetric assessment of the post-harvest indicators of edible mushrooms *C. indica* 2598, *C. aegerita* 2231, *P. citrinopileatus* 2161, and *P. pulmonarius* 2314.

4.3 Experimental evaluation of crop quality preservation features of *C. indica* 2598, *C. aegerita* 2231, *P. citrinopileatus* 2161, and *P. pulmonarius* 2314

4.3.1 Materials and methods

4.3.1.1 Spawn

Pure cultures of mushrooms were obtained by cutting pieces of trama from the inner parts of the carpophores and transferring them to agar medium with malt extract and incubated for 14 days at 25 °C. Pure cultures were deposited at the IBK Mushroom Culture Collection of the M. G. Kholodny Institute of Botany of the National Academy of Sciences of Ukraine, which is officially recognized as the national heritage of the country. They were maintained on 3 % malt extract agar medium and stored at 4±1 °C (*C. aegerita* 2231, *P. citrinopileatus* 2161, *P. pulmonarius* 2314), at 16±2 °C for *C. indica* 2598, because it is not thermoresistant strain. Some cultures days (*P. citrinopileatus* 2161, *P. pulmonarius* 2314) were incubated 7 at 24 °C, and at 30 °C for culture *C. indica* 2598. Only *C. aegerita* 2231 required 10 days under 24 °C for fulling Petry dish surface. Actively growing mycelia was used for mycelia spawn preparation, which contained barley, wheat, rape, flax, and chalk ($CaCO_3$) combined in the ratio 60:30:8:1:1 [38]. Pre-cooked barley and wheat, pre-soaked rapeseeds, flaxseeds, and chalk were properly mixed before loading (6 kg) into polypropylene

bags of size (570×470 mm), PP75/BEU6/X47-57 (Sac02, Belgium). The bags were sterilized at 128 °C, 1.8 atm for 3 h. Upon cooling, the sterile grain mixture was inoculated with mother spawn (0.5 % w/w), sealed, and incubated at 22 °C (*C. aegerita* 2231, *P. citrinopileatus* 2161, *P. pulmonarius* 2314) and 30±1 °C (*C. indica* 2598) for six or seven days, followed by shaking and thorough mixing to achieve uniform mycelia colonization throughout the bag. After 8±1 days for *P. citrinopileatus* 2161 and *P. pulmonarius* 2314, and 10±1 days for *C. indica* 2598 and *C. aegerita* 2231, the resulting spawn and was ready. Spawn of *C. aegerita* 2231, *P. citrinopileatus* 2161 and *P. pulmonarius* 2314 was cooling to 10±1 °C and after that placing in refrigerator and storing at 2±1 °C until use. Grain mycelium of *C. indica* 2598 stored at 15±1 °C.

4.3.1.2 Substrate

The substrate was made from barley straw, sunflower husk, sunflower husk pellets, rapeseeds, corn flour, and chalk combined in the ratio 30:40:70:20:17:1 and water content adjusted to 68±1 %. The substrate was packed into 580×480 mm polypropylene bags with four 20×480 mm filter strips located 150 mm apart on one side of the bag. The substrate was sterilized for 2 h at 125±1 °C, cooled under aseptic conditions to 28±1 °C, and inoculated with spawn (5 % w/w). The bags were sealed, and the spawn was carefully mixed in by shaking to achieve even distribution throughout the substrate. The average weight of each substrate bag inoculated with spawn was 3330±123 g. 30 bags with substate used for each treatment.

4.3.1.3 Incubation

The substrates with mushroom cultures were incubated under 24±2 °C and 65 % air relative humidity (RH) during different time for each cultivar *C. aegerita* 2231 at 28±3 days, *P. citrinopileatus* 2161 – 18±2 days, *P. pulmonarius* 2314 – 12±1 days to start of pinning. Illumination was not applicable. The substrates with *C. indica* 2598 were incubated at 28±2 °C, and the average temperature inside the substrate bags was to 34±1 °C. On the 19th day, the bags were transferred to the fruiting chamber, opened, leaving a 6–7 cm high rim and applicated 30 mm casing from peat moss, which was soaking to 75 % water content. The casing layer was moistened with water at the rate of 100 ml per 0.047 m^2 every 48 hours. After casing, the following microclimate parameters were maintained in the fruiting room: temperature 29±3 °C, RH=91±4 %, CO_2 content 1520±310 ppm, and illumination 150±30 lux.

4.3.1.4 Fruiting

The environment conditions for fruiting formation supported under optimal parameters for each cultivar. It was for *C. aegerita* 2231 and *P. citrinopileatus* 2161 at 16±2 °C, RH – 96±2 %. CO_2 – 1150±150 ppm (0.11 %), illumination was 150–200 lux during no less 8 hours per day. Fruiting of *P. pulmonarius* 2314 started without temperature changing at 24±2 °C, RH – 90±2 % CO_2 – 900±150 ppm. For *C. indica* 2598 fruiting the microclimate did not change after casing. In previous studies, a significant influence of the harvest time of 2 groups of *P. ostreatus* and *P. pulmonarius* strains on their technical, chemical and organoleptic indicators was revealed [31]. Therefore, for the studied cultivars, first of all, the possibility of harvesting at different stages of maturity was determined. The *P. pulmonarius* 2314 strain, which has been studied in previous experiments, has been designated as the baseline. Fruit bodies cropped in two maturates stage: before sporulation (technical) and when sporulation had started (biological). The total weight of the fruiting bodies obtained from each bag. The weight, the diameter (for *C. aegerita* 2231 and *C. indica* 2598, *P. citrinopileatus* 2161) and thickness of the caps, the height and width of caps for *P. pulmonarius* 2314 (because cap has oyster shape); the diameter and height of the stipe were measured for 100 fruiting bodies randomly. The biological efficiency (BE) was calculated for each flush as the total weight of fruiting body yield per flush divided by the dry weight of starting substrate (SW) multiplied by 100 % [39].

4.3.1.5 Storage and processing

The freshly harvested fruiting bodies were quickly cooled with active ventilation in a refrigerator with a temperature of 2±1 °C. Stored for no more than a day before processing: boiling or drying. After 12 hours of such storage, the fruiting bodies of *C. indica* 2598 were damaged, began to drain, lose elasticity, and the surface darkened (**Fig. 4.3, *f***). Therefore, in further studies, fresh *C. indica* fruiting bodies were used for processing, which were stored at a temperature of 14±1 °C for no more than a day. Boiled mushrooms (300 g) in boiling water for 5 minutes, cooled and let the water drain on a sieve, after 10 minutes the resulting sample was weighed. Drying was carried out by convection method at a temperature of 60±5 °C for 6 to 12 hours to a constant weight. Dried samples were ground to particles less than 1 mm and used for further analyses. It was stored for no more than 2 weeks at a temperature of 4±1 °C in a hermetically sealed container. The repetition of each experiment is threefold.

4.3.1.6 Nutritional and chemical analysis

Fresh fruiting bodies were dried at 45–50 °C until constant weight, followed by grinding to particles less than 1 mm in diameter. The resulting powder was further dried in an oven at 92 ± 2 °C to obtain absolute dry weight. The percentage moisture content in fruiting bodies was calculated as the difference in weight between fresh and absolute dry weight of fresh mushrooms multiplied by 100 %. The ash content was determined by weighing 3 g of absolute dry fruiting body powder into ceramic crucibles of known weight, burn in the oven (550 ± 10 °C) for three hours, and cooled in a desiccator. The difference in weight between the leftover and starting dry fruiting body material in the crucible is the ash content expressed in percentage. Total nitrogen was determined by Kjeldahl method multiplied by a factor of 4.38. The lipids content was determined by extraction from the mushroom sample (absolute dry) with petroleum ether as a solvent, using a Soxhlet apparatus (AOAC, 1995). The carbohydrate content was determined according to the formula: 100 – (percentage proteins, lipids, and ash combined).

4.3.1.7 Statistical data analysis

Statistical data analysis was performed using Microsoft Office Excel 2016 MSO (16.0.4266.1001). The ANOVA Single Factor was used for comparing variable data. Differences were considered significant at $p < 0.05$. The repetition of each experiment is threefold.

4.3.2 Morphological changes during technical and biological maturity

The external characteristics of the fruiting bodies changed significantly during the onset of sporulation (**Table 4.2**).

In all cultivars, the edge of the cap was thinned, but the pigmentation of its surface decreased to varying degrees, and the lamellae of the hymenal layer darkened. The flesh of the cap became looser with the onset of biological maturity. Common to all strains were changes in the structure of the legs: they became more rigid and fibrous.

The appearance of the baseline (control) *C. indica* 2598 and *P. pulmonarius* 2314 changed slightly with age (**Fig. 4.3**). It should be noted that due to the decrease in turgor in the pulp cells, the fruiting bodies *of C. indica* 2598 became less elastic, and when mechanically pressed during harvesting, slightly visible watery spots were

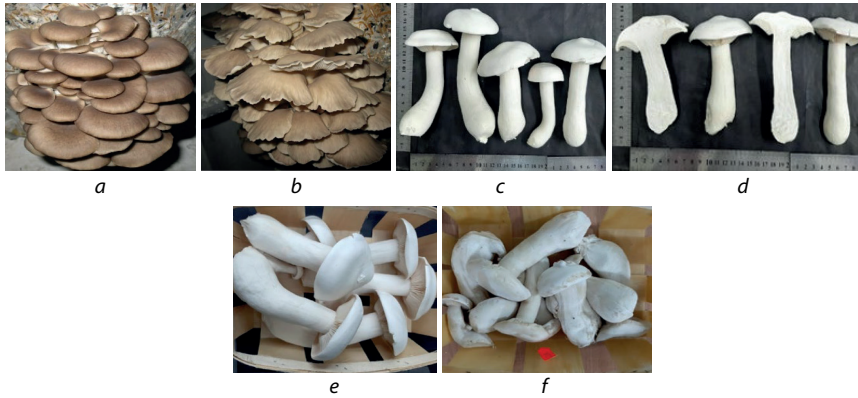
formed on the stems. In general, the qualitative characteristics of the fruiting bodies of these two strains in of varying degrees of maturity remained satisfactory.

Table 4.2 Morphological descriptions of mushroom crop with different maturities

Parameter	Maturity	Species and strains			
		Calocybe indica 2598	*Cyclocybe aegerita* 2231	*Pleurotus citrinopileatus* 2161	*Pleurotus pulmonarius* 2314
1	2	3	4	5	6
Cap shape	Technical	Round, convex, symmetrical, sometimes having a slight elevation in the center, and its edge is smooth and dense	Round, convex, with downturned edges, connected by a vail to the stipe	Rounded, with clear edges, and deepening in the center	Rounded, rarely slightly oystered, the width is always almost equal to the height, with even, firm edges
	Biological	Round, flattened, the edge is thin, sometimes with small cracks up to 1–3 mm deep	Round, flat or slightly convex, edges smooth, sometimes with remnants of a pieces of vail on the edges	Rounded, sometimes with a slightly offset center and wavy, brittle edges	Oyster, wider than height, edges loose, slightly wavy, sometimes curved upwards
Cap color	Technical	The color is milky white, matte, and free of any blemishes or tints	The color ranges from dark brown to bright brown, sometimes with a lighter edge and velvety	The color is yellow, but the center is more intense	The surface is uniformly gray-brown, with a slight lighter color at the stipe attachment point
	Biological	Milky with a slight yellowness, less saturated at the edge of the cap	Light brown – darker in the center and almost white on the edge	Light yellow at the edge, more intense in the center, sometimes with dark watery spots	Lighter shade compared to biological maturity, noticeable ripples in the form of darker and more loopy areas, especially along the edge of the cap
Hymenium color	Technical	Milky white, matte. The gills are translucent in the light	Pinkish-white, gills are translucent	Transparent white, with a slight boogie tint	White, with a slight beige tint
	Biological	Pinkish with a beige tint, intense	Brown, rich, velvety	Light beige, with a slightly pinkish tint	Beige, "dirty" due to slight unevenness

Continuation of Table 4.2

1	2	3	4	5	6
Stipe properties	Technical	Long, dense, elastic, but not fibrous, with no visible differences in density around the perimeter	Dense, elastic, does not break well, tightly connected to the cap	Dense but not rigid, with centric or slightly asymmetrical attachment to the cap	Short, fibrous, but not rigid, asymmetrical attachment to the cap, hymenium smoothly transitions to the stem
	Biological	The enlarged lower part is slightly compacted, at the point of attachment to the substrate	Fibrous, easily detached from the cap, covered with scales up to 1 mm	The loose tissue of the stipe becomes denser, especially around the perimeter	With age, it does not increase or thicken, does not become stiffer



a *b* *c* *d* *e* *f*

Fig. 4.3 Changes in mushrooms with age: *P. pulmonarius* 2314 fruiting clusters in the technical (*a*) and biological (*b*) maturity; *C. indica* 2598 whole (*c*) and cutting fruiting bodies (*d*); carpophores after day storage at 14±1 °C (*e*) and at 2±1 °C (*f*)

The fruiting bodies of *P. citrinopileatus* 2161 became brittle and crumbled at the base of the stalk. In the fruiting bodies of *C. aegerita* 2231, with the onset of biological maturity, the cover was torn, and the cap was easily separated from the stem during harvesting. The shedding of dark spores caused the surface to turn brown, which spoiled the appearance of the crop. Therefore, the cultivars *C. aegerita* 2231 and *P. citrinopileatus* 2161 should only be harvested at the stage of technological maturity. Increased temperatures during the fruiting period contribute to the acceleration of physiological processes in the fruiting bodies of fungi, which, accordingly, leads to

rapid ripening. Therefore, in order to preserve the quality of the crop, *P. pulmonarius* 2314 is harvested 2–3 times a day. It is possible to recommend the same approach when growing *C. indica* 2598.

The morphological features of the fruiting bodies were analyzed, the variability of which in the samples did not exceed 20 %, which indicates the satisfactory constancy of this indicator of the quality of the harvest for all studied varieties (**Table 4.3**).

Table 4.3 Morphological characteristics of fruiting bodies (technical maturity)

Species, strain	FB weight, g	FB height, mm	Stipe length, mm	Stipe diameter, mm	Cap diameter, mm
C. indica 2598	84.7±4.8	130.1±5.9	100.7±1.31	34.2±1.1	80.6±1.9
C. aegerita 2231	5.5±0.6	78.2±2.3	68.6±2.1	8.3±0.3	28.6±1.2
P. citrinopileatus 2161	10.5±0.9	74.6±1.7	45.5±2.1	12.2±0.7	51.2±2.3
P. pulmonarius 2314	3.5±0.2	38.5±1.0	18.6±0.8	5.6±0.2	41.1±1.4

The fruiting bodies of *C. indica* 2598 had the highest weight, which ranged from 20 to 380 g in isolated cases, while more than 80 % of the crop consisted of fruiting bodies weighing from 55 to 127 g. Let's assume that such differences will make it possible to influence the visual perception of the assortment of mushrooms on supermarket shelves and, thus, attract the attention of customers.

4.3.3 Nutritional value of fruiting bodies

Cultivars recommended for summer cultivation significantly ($p<0.05$) differed in a higher content of dry substances in fruiting bodies in comparison with the conditional "winter" group of studied strains (**Table 4.4**).

Table 4.4 Chemical composition of cultivars

Species, strain	Dry matter, %	Contents, % (DW)			
		Crude proteins	Lipids	Carbohydrates	Ash
C. indica 2598	11.02±0.51	12.31±0.37	5.27±0.66	74.75±0.83	7.63±0.21
C. aegerita 2231	8.49±0.49	19.36±0.17	2.59±0.08	70.73±0.04	7.33±0.25
P. citrinopileatus 2161	8.54±0.05	21.46±0.51	1.56±0.23	68.33±0.31	8.64±0.08
P. pulmonarius 2314	11.17±0.22	18.75±0.63	1.12±0.13	72.81±0.27	7.11±0.03

At the same time, there were practically no differences in this indicator within these conditional groups. The fruiting bodies of *P. citrinopileatus* 2161 (21.46±0.51 %) had the highest protein content, while *C. indica* 2598 had the lowest protein content in the experiment (12.31±0.37 %). *C. indica* 2598 had the highest fat content (5.27±0.66 %), which is 4.7 times higher than that of *P. pulmonarius* 2314, which had the lowest score (1.12±0.13 %), and 2 times *C. aegerita* 2231. The total carbohydrate content ranged from 74.75±0.83 % (*C. indica* 2598) to 68.33±0.31 % (*P. citrinopileatus* 2161), however, no significant differences were found between other strains. The highest ash content among the studied cultivars was found in the fruiting bodies of *P. citrinopileatus* 2161 (8.64±0.08 %), while the lowest in *P. pulmonarius* 2314 (7.11±0.03). The ratio protein/fat/carbohydrate nutrients were different for the studied strains 2:1:14 (*C. indica* 2598), 7.5:1:27 (*C. aegerita* 2231); 14:1:44 (*P. citrinopileatus* 2161); 17:1:65 (*P. pulmonarius* 2314) and but all had in common a low-fat content. It should also be taken into account that the amount of easily digestible carbohydrates in mushrooms does not exceed 0.1 % [40]. Such a balance makes it possible to use mushrooms and products of their processing in low-calorie diets that meet the general trends in the development of the modern food industry.

4.3.4 Determination of the yield coefficient of semi-finished products in different processing options

To establish an integral quality indicator that incorporates the costs of obtaining the final product, it is necessary to have a precise forecast of losses at every stage of raw material processing. For the studied strains, the greatest losses at the purification stage were found during the processing of the *C. indica* 2598 crop – 7.3 % and *P. citrinopileatus* 2161 – 7 %, while during the cleaning of the clusters *P. pulmonarius* 2314 lost no more than 1 % of the weight of the collected mushrooms (**Table 4.5**).

Table 4.5 Yield coefficients of semi-finished mushroom products processing stages

Species, strain	Cleansing	Boiling	Drying
C. indica 2598	0.927±0.021	0.798±0.009	0.088±0.007
C. aegerita 2231	0.956±0.004	0.803±0.006	0.092±0.005
P. citrinopileatus 2161	0.930±0.011	0.853±0.019	0.098±0.006
P. pulmonarius 2314	0.991±0.017	1.095±0.028	0.090±0.003

Let's attribute this to the lack of a cluster base in this strain, which makes it possible to easily separate the fruiting bodies from each other for pickling or drying. The increased weight loss of *C. indica* 2598 during cleaning depends on the need to remove the remaining casing soil from the base of the stem. Short-term boiling of *P. pulmonarius* 2314 mushrooms was accompanied by a slight increase (up to 1 %) in the mass of processed raw materials due to moisture retention by loose tissues of fruiting bodies. Perhaps this is due to the high content of water-soluble components, the need to determine which is dictated by the possibility of using mushroom decoctions to make broths or obtain extracts. The highest loss rate is typical for the processes of obtaining dry semi-finished mushroom products. Thus, the drying of *C. indica* 2598 led to a decrease in the weight of the crop by 91.2 % (the maximum indicator in the experiment), and the smallest losses were recorded when the fruiting bodies of *P. citrinopileatus* 2161 (90. 2 %) were dried. In general, the highest losses of raw materials were identified in the processing of the *C. indica* 2598 crop, and the lowest in the case of the control strain.

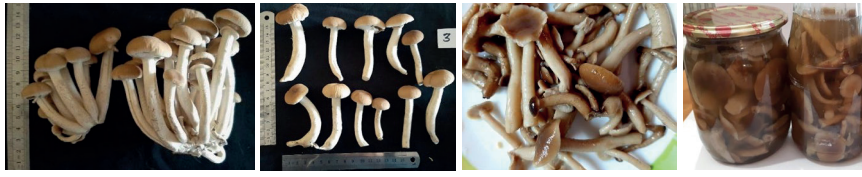
It is necessary to note the change in the organoleptic characteristics of the studied strains after boiling. For example, the fruiting bodies of *P. citrinopileatus* 2161 changed their bright yellow color to beige (**Fig. 4.4**), which indicates that it is inexpedient to use this cultivar for the preparation of marinades in transparent glass containers. However, the boiled fruiting bodies of this strain acquired a pleasant aroma of seafood, and the broth turned a pleasant yellow color. Such changes, in our opinion, restaurateurs will be interested in making main dishes: soups, side dishes, as well as minced meat, fillings, pâtés. The powder obtained from the dried mushrooms of this strain had pleasant yellow hue and aroma, which makes it possible to use it as a natural coloring and flavoring agent in the creation of sauces, pasta and bakery products.

The fruiting bodies of *C. aegerita* 2231 did not lose their color and elasticity after boiling. "Crispy", with a rich mushroom aroma – they were most suitable for pickling (**Fig. 4.5**). At the same time, minced meat from this raw material was tender and elastic but had a dark brownish tint. Dried mushrooms were easily crushed, the powder had a brownish hue, a pleasant mushroom aroma. Semi-finished products obtained from the crop *P. pulmonarius* 2314 had similar organoleptic characteristics. After boiling, the fruiting bodies did not lose pigmentation on the surface of the cap, remaining elastic, and were easily chewed. The consistency of the minced meat was homogeneous, like minced meat from *C. aegerita* 2231. The aroma was neutral, unsaturated, which, in our opinion, makes it possible to use such raw materials as a filler and a partial replacement of the meat component in cutlets, sausages and pâtés. It should be noted the high moisture-holding capacity of such a semi-finished product. Powder from *P. pulmonarius* 2314 had a light gray hue and a faint, barely perceptible aroma. Therefore, the harvest of these mushrooms is most suitable

for pickling, the manufacture of meat and vegetable semi-finished products and finished products, but to a lesser extent for sauces and fillings.

a *b* *c* *d*

Fig. 4.4 *Pleurotus citrinopileatus* 2161 clusters (*a*) and carpophores (*b*) and changing of carpophore color after of 3 minutes (*c*) and 10 minutes (*d*) boiling



a *b* *c* *d*

Fig. 4.5 *Cyclocybe aegerita* 2031 clusters (*a*) and carpophores (*b*) and carpophores after of 10 minutes boiling (*c*) and as pickles with 2 % acetic acid (*d*)

The large fruiting bodies of *C. indica* 2598 must be crushed before processing, which negatively affects the visual perception of marinades. It is also necessary to consider that heat treatment for more than 5 minutes makes the flesh of these mushrooms tough. The minced meat was coarse-grained, dense, and difficult to mix with other ingredients. The most successful method was the quick blanching of slices or bars with a thickness of no more than 5 mm, instant salads, sauces and first courses. The powder from the dried fruiting bodies did not have a pronounced mushroom aroma, it was fine-grained, almost airy. Thus, the processing of the crop of this cultivar can be more successful in the direction of the production of blanched semi-finished products for restaurants and cafes, as well as powders used in the future to produce sauces, pasta and bakery products.

Conclusions

In recent decades, mushrooms, due to their special functional properties, are confidently included in the daily diet of people who consider the possibilities of

nutrition to improve their health. Therefore, the production and consumption of mushrooms, as well as products of their processing, is growing rapidly, and the range of species available on the market is actively expanding. The organization of a system for assessing the quality of the mushroom harvest and products made from it is a complex process, since, in addition to food safety, it must consider the peculiarities of the morphology and physiology of the cultivars, individual changes during storage and heat treatment process, and, in addition, constantly changing market preferences. Main indicators for a complex estimate of mushroom crop quality for future processing procedures include safety characteristics, organoleptic indicators, dry matter (or water content), and biomass texture (dense, fibrous, delicate). One way to solve the problem of preserving the quality of mushroom crop, which has a limited shelf life, is to expand the ways of its processing. This investigation presents the results of the study of morphological, technical, and chemical indicators of the harvest and processed products of edible fungi *Calocybe indica* (milky mushroom), *Cyclocybe aegerita* (pioppino), *Pleurotus citrinopileatus* (golden oyster mushroom), and *Pleurotus pulmonarius* (lung oyster mushroom). The qualimetric assessment of the post-harvest characteristics of strains from the domestic collection makes suggests high prospects for use the studied mushrooms for visual attraction customers to expand the range of mushroom products on supermarket shelves. The proposed seasonal approach to the cultivation of the studied strains considers the possibility of reducing the cost of the mushroom crop. A comprehensive analysis of the proposed qualimetric assessment and the quality features of the cultivated mushrooms studied, depending on the methods of further processing, indicates the prospects of this area of research and the feasibility of bringing other species of exotic cultivated mushrooms to the market.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 5

Technology of multilayer and glazed fruit and vegetable chips

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Abstract

Fruit and vegetable chips are a growing segment of the global snack market. These chips are an alternative to high-calorie potato chips. Fruit and vegetable chips can be a useful snack between main meals, allowing the human body to get the necessary vitamins, macro and micro elements. No oil is used in the production of fruit and vegetable chips, and they do not contain added sugar, artificial colours and flavors. Instead, these chips contain beneficial substances that are rich in fresh fruits and vegetables, albeit in smaller quantities.

Because fruits and vegetables lose valuable nutrients during storage, they must be processed into high-quality fruit and vegetable chips. Blanching, immersion in various solutions and osmotic dehydration of the plant raw materials before drying are used to reduce the loss of nutrients during the production of fruit and vegetable chips and to preserve the taste, smell and colour of the plant raw materials in the finished product. The developed technologies of multilayer and glazed fruit and vegetable chips allow consumers to obtain an innovative product with original taste properties and nutritional composition. The modes of the proposed technology of multilayer chips allow producers to preserve as much as possible the taste and colour of plant raw materials (fruits and vegetables) in the finished product, as well as nutrients. As a result of combining different types of plant raw materials (vegetables, fruits, seeds) it is possible to obtain a wide range of multilayer chips with different tastes that can satisfy the preferences of different categories of consumers. By combining plant raw materials, manufacturers can also balance the nutrient content of the chips and obtain a functional product for specific target groups of consumers.

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The proposed chocolate-glazed (with black, white or milk chocolate) multilayer chips are a promising product in the sweet chips segment. The use of chocolate makes it possible to balance the nutritional value of the multilayer chips, and the addition of freeze-dried plant powders (fruits, vegetables, berries) or their combination to the glaze enriches the product with vitamins, macro and micro elements, and gives the chips new flavors and colours.

Keywords

Fruit chips, vegetable chips, multilayer chips, glazed chips, technology of fruit chips, technology of vegetable chips, healthy chips, properties of chips.

5.1 Introduction

Snacking is the modern trend in eating patterns, defined as eating outside of the main meals (breakfast, lunch and dinner). The popularity of snacks is due to urbanization, accelerated pace of life, economic and social factors, etc. If the energy intake from a meal is less than 15 % of the recommended daily energy intake, it is a snack [1]. In the global market, a significant segment of snacks consists of salty and sweet foods that can contribute "empty" and excess calories that do not provide essential nutrients to help consumers meet their nutritional needs [2]. In addition, snacks are often considered a major contributor of fat and simple carbohydrates to the diet [3]. This has led most consumers to believe that snacks are unhealthy foods. Also, snack food consumption is often associated with the socioeconomic status of consumers. Low socioeconomic status is thought to lead to the consumption of foods that are low in nutrients but high in energy [4]. But proper snacking has a number of health benefits related to appetite control and weight management [5]. Eating nutritionally balanced snacks with vitamins and minerals between main meals may contribute to meet the recommended daily intake of healthy foods [1]. To achieve a positive effect from snacking, it is important to plan snacks properly and consider their energy value, taking into account a person's age and lifestyle.

The most popular snack in the world is potato chips, which are prepared by deep-frying raw solid potato slices or pre-cooked and dried potatoes in the form of flakes or powder with starch in vegetable oils [6]. Dried onion, garlic, parsley, celery and dill, mushrooms, cabbage, carrot, salt, etc. are added to the potato chips to enhance the taste and flavor. Spicy and aromatic parts of plants (seeds, roots, bark, leaves, flowers, etc.) are also used to improve the sensory properties of potato chips.

During deep-frying, the physical, chemical and sensorial characteristics of potato chips are modified [7]. In fried foods, the amount of fat reaches 1/3 of the

total weight of the food, which can pose a risk to human health [8]. Methods to reduce oil absorption by fried foods have been developed [7, 9]: soaking potato slices in NaCl solution; frying potato slices in vacuum; blanching potato slices before frying; microwave treatment of potato slices; drying or baking potato slices before frying; using hydrocolloids added to the breading coating to create a barrier against oil absorption.

When potato chips are fried at high temperatures (170–190 °C), acrylamide, a potentially carcinogenic compound, is also formed [10]. Acrylamide content in potato chips can range from 211 to 3515 μg kg^{-1} [11]. During frying in oil, vitamin C losses in potatoes can reach 83.35 %, depending on the heating level and time [12]. Changes in the mineral content of fried potatoes are caused by water loss. Due to the high starch content of potatoes, potato products are among the products with a high Glycemic Index (GI), in particular, the Glycemic Index of potato chips is 77 ± 4 [13].

The driving force in the snack market is the development of allergen-free, vegan and gluten-free natural products with reduced calories, sodium and saturated and trans fats [14]. Consumers also choose snacks based on price, brand, taste and packaging that extends shelf life without compromising quality. Fruit and vegetable snacks are growing in popularity due to changing lifestyles and a focus on healthy eating, especially products fortified with vitamins, minerals, antioxidants and plant extracts that are low in fat, salt and sugar and free of synthetic food dyes, additives and GMOs. Chips made from vegetables, fruits, berries, and grains are one of the most common types of plant-based snacks. Drying, frying, baking, extruding, or a combination of these techniques are used to produce plant-based chips.

The development of new vegetable and fruit chips, with the possibility of combining different plant-based ingredients in one product, is promising for the expansion of the snack range.

5.2 Nutritional value of plant-based ingredients for chips

Vegetables, fruits, berries, seeds and their processed products are plant-based ingredients for chips. Various types of chocolate, a product made from roasted and ground cocoa beans, are used to glaze the chips. Fruits, vegetables and other plant-based ingredients in chips have high nutritive value in both raw and processed forms. This section provides a brief description of the nutritional value of certain types of plant raw materials used in the production of fruit and vegetable chips and chocolate-glazed chips.

5.2.1 Apple

Apple fruits are a source of organic acids, vitamins and minerals (mg 100 g^{-1}) [15, 16]: malic acid – 919 ± 109; citric acid – 21.5 ± 3.7; ascorbic acid – 24.14 ± 0.18; sodium (Na) – 3.76–23.70; potassium (K) – 112.3–795.1; calcium (Ca) – 4.43–26.39; magnesium (Mg) – 7.99–21.82; iron (Fe) – 0.28 ± 0.02; zinc (Zn) – 0.19 ± 0.02; manganese (Mn) – 0.04 ± 0.0; copper (Cu) – 0.05 ± 0.0. Apple fruits have a high sugar content of 8.9–15.0 % and water content of 76.7–88.4 %, and also contain soluble dry matter of 10.8–16.5 % and ash in the amount of 1.6–2.8 % [15]. The polyphenol content of apple fruit is in the range of (mg 100 g^{-1} DW) [17]: flesh – 9.6–41.6; peel – 36.39–256.19. For the production of chips, it is recommended to use sour and sweet-sour varieties of apples with soluble sugar content of 13.0–14.7 %. The nutritional value of apple is as follows (g 100 g^{-1}) [18]: protein – 0.3; fat – traces; carbohydrates – 12.0; fructose – 5.6; glucose – 1.8; sucrose – 2.6.

5.2.2 Pear

Pears are a nutrient-rich fruit, containing the following nutrients (%) [19]: water – 84.9; protein – 0.3; fat – 0.1; carbohydrates – 14.4; dietary fiber – 1.9. The mineral content of pears is in the range of (mg kg^{-1}) [20]: sodium (Na) – 3.2–138.6; potassium (K) – 2685.1–9212.7; calcium (Ca) – 303.1–2424.9; magnesium (Mg) – 16.0–765.3; iron (Fe) – 6.0–52.0; zinc (Zn) – 2.8–16.9; manganese (Mn) – 1.2–6.8; copper (Cu) – 1.5–11.6; phosphorus (P) – 353.3–1799.8. The content of vitamin C in pears is in the range of (mg 100 g^{-1}) [21]: flesh – 9.1–29.7; peel – 9.5–35.9. Other vitamins are contained in this amount (mg 100 g^{-1}) [18]: vitamin E (α-tocopherol) – 0.12; thiamin – 0.012; riboflavin – 0.025; niacin – 0.157; pyridoxine – 0.028. The pear peel has a higher phenolic content than the pear flesh [21]. The sugar content of pears is as follows (g 100 g^{-1}) [18]: fructose – 5.3; glucose – 4.2; sucrose – 1.2; total – 10.7.

5.2.3 Carrot

Carrot is a source of carbohydrates and minerals; it contains the following nutrients (%) [22]: water – 86–89; protein – 0.7–0.9; fat – 0.2–0.5; carbohydrates – 6.0–10.6; dietary fiber – 1.2–2.4; ash – 1.1. The mineral and vitamin content of carrots is as follows (mg 100 g^{-1}) [22]: sodium (Na) – 40.0; potassium (K) – 240.0; calcium (Ca) – 34.0; magnesium (Mg) – 9.0; iron (Fe) – 0.1; zinc (Zn) – 0.2;

copper (Cu) – 0.02; phosphorus (P) – 25.0; thiamine – 0.04; riboflavin – 0.02; niacin – 0.2; vitamin C – 4.0. In different varieties of carrots, the content of α-carotene is in the range of 530–35833 μg 100 g^{-1}, and the content of β-carotene is in the range of 1161–64350 μg 100 g^{-1} [23].

5.2.4 Table beet

Table beets contain folic acid and have a high concentration of betalain pigments, which are powerful antioxidants. Also, table beets contain the following nutrients (%) [24]: water – 87.4±0.3; fat – 0.3±0.1; protein – 1.35±0.2; carbohydrates – 7.59±0.4; crude fiber – 1.9±0.2; ash – 1.4±0.2. The total sugar content in table beets varies between 21.03–31.58 g kg^{-1} [25]. The mineral and vitamin content of table beets is as follows (mg 100 g^{-1}) [24]: sodium (Na) – 72.6; potassium (K) – 30.1; calcium (Ca) – 12.2; iron (Fe) – 0.75; zinc (Zn) – 0.21; copper (Cu) – 0.09; vitamin B_6 – 0.067; niacin – 0.334; vitamin C – 7.2.

5.2.5 Zucchini

The total sugar content of zucchini varies between 3.7–3.9 g 100 g^{-1}, in particular, fructose – 1.8–1.9 g 100 g^{-1}, glucose – 0.9–1.0 g 100 g^{-1}, sucrose – 0.9–1.1 g 100 g^{-1} [26]. The content of vitamin C in zucchini is in the range of 7.6–8.0 mg 100 g^{-1}, phenolic acids – 37.9–40.9 μg g^{-1}, flavonoids – 4.2–4.4 μg g^{-1} [26]. The mineral content of zucchini is as follows (mg 100 g^{-1} DW) [27]: potassium (K) – 2999.2–4660.0; calcium (Ca) – 243.7–359.0; iron (Fe) – 3.4–7.3; zinc (Zn) – 4.0–4.5; copper (Cu) – 0.36–0.90; phosphorus (P) – 541.2–600.0; magnesium (Mg) – 243.7–319.0; manganese (Mn) – 2.3–2.7.

5.2.6 Flax seeds

The chemical composition of flax seeds may vary depending on the characteristics of the variety and growing conditions. The chemical composition of flax seeds is as follows (%) [28]: water – 6.99±0.24 %; protein – 21.76±0.58 %; fat – 42.41±1.01 %; carbohydrates – 26.11±0.80 %; ash – 4.00±0.25 %. Flax seeds are also a source of dietary fiber (40 g 100 g^{-1}), α-linolenic acid (22.8 g 100 g^{-1}), linoleic acid (5.9 g 100 g^{-1}) and oleic acid (7.3 g 100 g^{-1}) [29]. The mineral and vitamin content of flax seeds is as

follows (mg 100 g^{-1}) [29]: sodium (Na) – 27.0; potassium (K) – 831.0; calcium (Ca) – 236.0; iron (Fe) – 5.0; zinc (Zn) – 4.0; copper (Cu) – 1.0; phosphorus (P) – 622.0; magnesium (Mg) – 431.0; manganese (Mn) – 3.0; thiamine – 0.53; riboflavin – 0.23; niacin – 3.21; ascorbic acid – 0.50; pyridoxine – 0.61; pantothenic acid – 0.57; folic acid – 0.112. Due to its chemical composition, flaxseed is an important functional ingredient in the diet.

5.2.7 Freeze-dried vegetable and fruit-berry powders

To improve the colour, taste and nutritional value of foods, freeze-dried vegetable and fruit-berry powders are added to them as ingredients. The mineral content of freeze-dried plant powders (strawberry, raspberry, apricot, blackcurrant, pumpkin) is in the range of (mg 100 g^{-1}) [30]: sodium (Na) – 62.7–152.2; potassium (K) – 703.6–1610.7; calcium (Ca) – 124.3–223.3; iron (Fe) – 3.8–11.6; zinc (Zn) – 2.4–5.3; copper (Cu) – 34.0–464.1; phosphorus (P) – 115.7–340.1; magnesium (Mg) – 73.1–170.4; manganese (Mn) – 0.3–1.4. The content of phenolic compounds in freeze-dried plant powders (blueberry, raspberry, blackberry, pomegranate, table beet) is as follows (mg 100 g^{-1} DW) [31]: catechin – 10.09–35.41; epicatechin – 48.34–58.50; anthocyanins – 138.74–32933.63. Freeze-dried plant powders (carrot, beet, pumpkin, apple, raspberry, apricot) contain the following nutrients (%) [32]: protein – 3.2–9.2; fat – 0.0–1.0; carbohydrates – 52.3–73.0.

5.2.8 Chocolate

There are many types of chocolate (dark, milk, and white) with varying content of cocoa, cocoa butter, and milk. The nutritional composition of chocolate depends mainly on the cocoa content [33]:

– white chocolate (g 100 g^{-1}): protein – 5.87; fat – 32.1; carbohydrates – 59.2;

– milk chocolate (g 100 g^{-1}): protein – 7.65; fat – 29.7; carbohydrates – 59.4;

– dark chocolate with 45–59 % cocoa content (g 100 g^{-1}): protein – 4.88; fat – 31.3; carbohydrates – 61.2.

The level of minerals in different types of chocolate with different cocoa content varies widely:

– white chocolate (mg 100 g^{-1}) [33]: potassium (K) – 286; calcium (Ca) – 199; iron (Fe) – 0.24; zinc (Zn) – 0.45; phosphorus (P) – 176; magnesium (Mg) – 12; manganese (Mn) – 0.008; selenium (Se) – 0.0045;

– milk chocolate (mg 100 g^{-1}) [34]: sodium (Na) – 72.91±1.48; potassium (K) – 379.05±10.94; calcium (Ca) – 180.43±3.00; iron (Fe) – 1.19±0.03; zinc (Zn) – 0.94±0.04; copper (Cu) – 0.31±0.00; phosphorus (P) – 198.91±2.72; magnesium (Mg) – 52.28±2.03; manganese (Mn) – 0.31±0.00; selenium (Se) – 0.06±0.01;

– dark chocolate with 60–90 % cocoa content (mg 100 g^{-1}) [34]: sodium (Na) – 3.30–5.20; potassium (K) – 465.55–720.11; calcium (Ca) – 64.33–90.83; iron (Fe) – 9.73–11.24; zinc (Zn) – 2.24–3.52; copper (Cu) – 1.43–2.02; phosphorus (P) – 221.80–396.51; magnesium (Mg) – 158.78–252.21; manganese (Mn) – 1.65–2.05; selenium (Se) – 0.08–0.10.

The vitamin content of different types of chocolate is as follows (mg 100 g^{-1}) [33]:

– milk chocolate (mg 100 g^{-1}): thiamine – 0.112; riboflavin – 0.298; niacin – 0.386; vitamin E – 0.51;

– dark chocolate with 45–59 % cocoa content (mg 100 g^{-1}): thiamine – 0.025; riboflavin – 0.05; niacin – 0.725; vitamin E – 0.54;

– white chocolate (mg 100 g^{-1}): thiamine – 0.063; riboflavin – 0.282; niacin – 0.745; vitamin E – 0.96.

Milk chocolate contains between 0.05 % and 0.17 % caffeine, while dark chocolate contains between 0.23 % and 0.31 % [35].

5.3 Materials and methods

5.3.1 Materials and laboratory equipment

The developed compositions of multilayer fruit and vegetable chips containing apples, carrots, pears, table beets, zucchini, flax seeds, chocolate (dark, milk, and white), freeze-dried plant powders (mango, bilberry, strawberry, blueberry, raspberry, currant) were examined. Fruits, vegetables, freeze-dried plant powders, flax seeds, and chocolate were purchased from a local supermarket (Lutsk, Ukraine). The cocoa content in the chocolate (chocolate chips) was as follows: white chocolate – 31 %; milk chocolate – 38 %; dark chocolate – 70.5 %. Samples of multilayer chips and multilayer glazed chips were prepared according to the developed technologies.

During the study, the following laboratory equipment was used: GORENJE Slicer R 506 E; Morphy Richards Intellisteam Food Steamer 470006; Dehydrator Excalibur 4926T Black; Hamilton Beach Fresh Grind Electric Coffee Grinder; Esperanza Electric Hot Plate EKH008; Laboratory Drying Cabinet SNOL-250/350; Thermometer Testo 405V1; Laboratory Balances FEN-V2003; IRAffinity-1S Spectrometer. The study was conducted in the laboratory of the Lutsk National Technical University (Ukraine).

5.3.2 Methods

5.3.2.1 Moisture content and nutritional value determination

Moisture content of samples of multilayer chips was determined by standard method (AOAC Official Method) [36]. The moisture content of dried multilayer chips of all compositions (without glaze) ranged from 6.0 % to 8.0 %.

The protein, fat and carbohydrate contents were determined by the methods described in [37].

The determination of the mineral content of the developed chips consisted of two steps. In the first step, the determination of mineral content in samples of dried apple, carrot, pear, table beet, zucchini, and flax seeds, chocolate (dark, milk, and white), freeze-dried powders (mango, bilberry, strawberry, blueberry, raspberry, currant) was carried out by the technique of analysis by spectrophotometry plasma emission [34]. In the second step, the mineral content of the chips was determined by calculation, taking into account the mineral content of the dried components of the chips and their ratio in the finished product.

5.3.2.2 Sensory analysis and quality evaluation method

The sensory properties (appearance, colour, taste, smell and consistency) of multilayer chips and multilayer glazed chips were evaluated by experts according to the methodology [38] on a five-point scale (5 points – the quality is excellent; 4 points – the quality is good; 3 points – the quality is satisfactory; 2 points – the quality is poor (barely acceptable); 1 point – the quality is very poor). In addition to scoring the sensory properties of compositions of multilayer chips and multilayer glazed chips, experts gave their verbal description.

The weighting coefficients of the sensory properties of the examined multilayer chips were determined by the ranking method based on the results of an expert survey. The quality index Q of the samples of multilayer chips and multilayer glazed chips were determined by the expert method [38] and calculated by the Equation:

$$Q = \sum_{i=1}^{n} \frac{m_i q_i}{q_{bi}}, \tag{5.1}$$

where m_i is the weighting coefficient of the sensory properties of multilayer chips and multilayer glazed chips; q_i is the mean value of the sensory property of multilayer

chips and multilayer glazed chips (points); q_{bi} is the base value of the sensory property of multilayer chips and multilayer glazed chips (for all sensory properties the base value is 5 points).

5.3.2.3 Determination of the colour of the multilayer glazed chips

The colour of the multilayer glazed chips was determined using the camera of the Xiaomi Redmi Note 8 Pro smartphone (China) and the Color Detector & Catcher mobile application, using the RGB additive colour model. The colour of multilayer chips was not determined because different layers of chips had different colours, which is characteristic of the colours of dried raw materials.

5.3.2.4 Calorie content determination

The calorie content of multilayer chips and multilayer glazed chips was calculated by the Equation:

$$E = 4P + 9F + 3.75C, \tag{5.2}$$

where E is calorie content (kcal 100 g^{-1}); 4, 9, 3.75 are calories per 1 g of protein, fat, and carbohydrate, respectively (kcal); P, F, C are the mean amounts of protein, fat and carbohydrates, respectively, per 100 g of multilayer chips and multilayer glazed chips (g 100 g^{-1}).

5.3.2.5 Statistical analysis and calculations

All data reported as mean ± standard deviation (SD). Statistical analysis and calculations were conducted using the Mathcad 14 software.

5.4 Technologies of multilayer and glazed fruit and vegetable chips

The technology of multilayer fruit and vegetable chips is shown in **Fig. 5.1**. In order to separate the damaged and spoiled fruits, they are sorted. High quality, ripe fruits and vegetables are washed and peeled as needed. For the base layer of chips,

washed vegetables or fruits are sliced into 2–3 mm thick slices. During calibration, small and damaged slices are separated. Solid slices are blanched in steam at a temperature of 85–95 °C for 120–180 s.

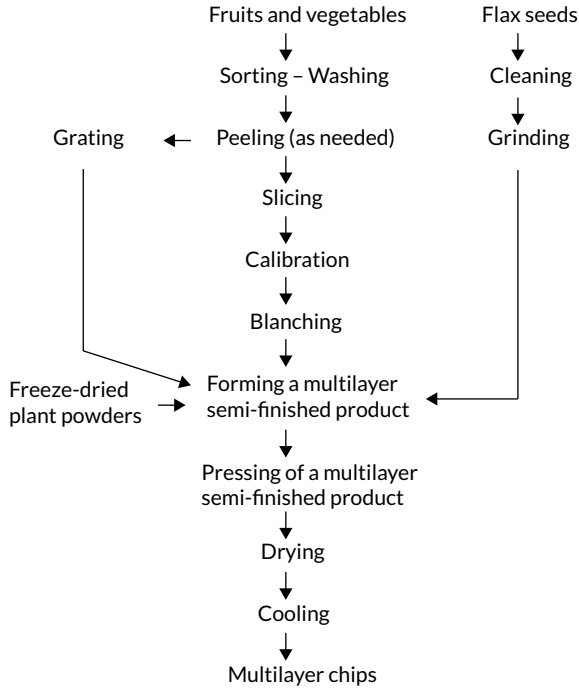

Fig. 5.1 Flowchart of technology of multilayer fruit and vegetable chips

Flax seeds are cleaned to remove impurities and ground to a fraction size of less than 2 mm. Some fresh fruits and vegetables are grated after washing. After the preparation of plant raw materials, multilayer semi-finished products are formed. For this reason, blanched slices of fruits and vegetables are breaded on one side in freeze-dried plant powder or powder mixture, and also breaded in crushed flax seeds. Over the layer of crushed flax seeds, a 2–3 mm thick layer of grated fruit or vegetables or both is formed. The formed multilayer semi-finished product is pressed and dried at a temperature of 63–70 °C to a moisture content of 5–8 %. The drying time can be 6–10 hours, depending on the plant raw material and its initial moisture content. In this regime of hot air drying, the useful substances contained in the plant raw

materials are preserved with the minimum loss in the finished product. Increasing the temperature of air drying causes an increase in the loss of nutrients and deterioration of the quality of the dried product, especially the quality of dried plant products deteriorates at a drying temperature of 80–95 °C [39]. Dried multilayer chips are cooled. Multilayer fruit and vegetable chips must be stored in a closed package at an air temperature of 0–20 °C and an air humidity of 75 % or less.

The technology of chocolate-glazed multilayer chips with freeze-dried plant powder or powder mixture is shown in **Fig. 5.2**.

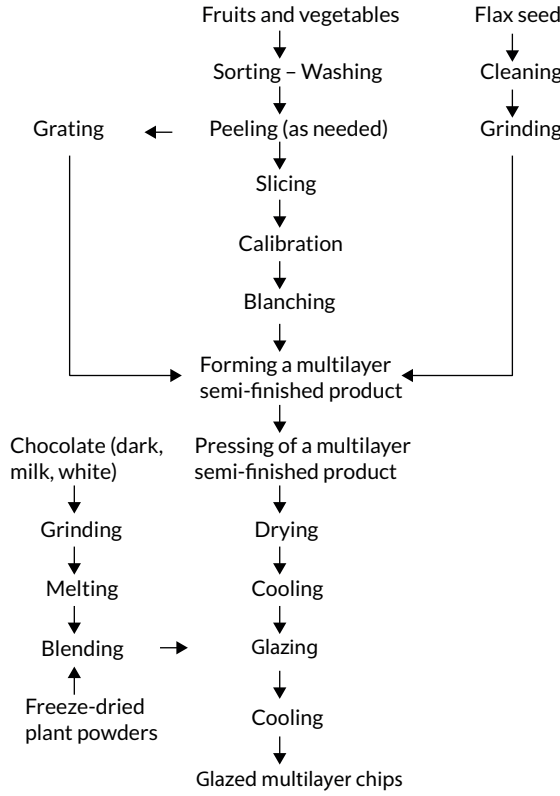

Fig. 5.2 Flowchart of technology of glazed multilayer fruit and vegetable chips

The preparation of plant raw materials is similar to the technology of multilayer chips. Blanched fruit and vegetable slices are breaded on one side in crushed

flax seeds. Then, a 2–3 mm thick layer of grated vegetables and fruits is formed over the layer of crushed flax seeds. The multilayer semi-finished product is pressed and dried at a temperature of 63–70 °C to a moisture content of 5–8 %. The dried multilayer semi-finished product is cooled.

Chocolate (white, dark, milk) is ground and melted. Freeze-dried plant powder or a powder mixture is blended with melted chocolate. The content of freeze-dried plant powder in the chocolate glaze does not exceed 10 %. The cooled semi-finished product is glazed on both sides in chocolate mass with plant powder. Chopped nuts may be sprinkled on both sides of the multilayer glazed chips. The finished product is cooled to the temperature of 15–20 °C. The storage conditions for chocolate-glazed multilayer chips are the same as for unglazed chips.

5.5 Characteristic of multilayer fruit and vegetable chips

5.5.1 Sensory properties of multilayer fruit and vegetable chips

The developed multilayer fruit and vegetable chips are shown in **Fig. 5.3** (samples of chips are marked as follows: A – solid apple slice; P – solid pear slice; T – solid table beet slice; Ma – mango powder; F – crushed flax seeds; Ag – grated apple; C – grated carrot; Pu – grated pumpkin; B – bilberry powder; Bl – blueberry powder; R – raspberry powder; S – strawberry powder). The appearance of the samples from the base layer side and their cross-section are also shown in **Fig. 5.4**. The base layer of the multilayer chips was a solid slice of apple, pear or table beet. Freeze-dried powders of mango, strawberry, bilberry, blueberry and raspberry were used to bread blanched apple, pear and table beet slices. The apple, pear and table beet slices were also breaded on one side with crushed flax seeds. Grated apple, carrot and pumpkin were used for the top layer of the multilayer chips.

The main sensory indicators of multilayer fruit and vegetable chips are appearance, colour, taste, smell and consistency. The results of the expert evaluation of the sensory properties of multilayer fruit and vegetable chips on a five-point scale are presented in **Table 5.1**.

Multilayer chips had different shapes. The shape of the chips depended on the fruits and vegetables used for the base layer of the chips and the direction in which they were cut. Some multilayer chips had a hole in the central part from the cut core of a fruit containing seeds or pips (e. g. apples, pears). As a result of drying, the base layer of the chips was deformed, resulting in a wavy surface of the finished product.

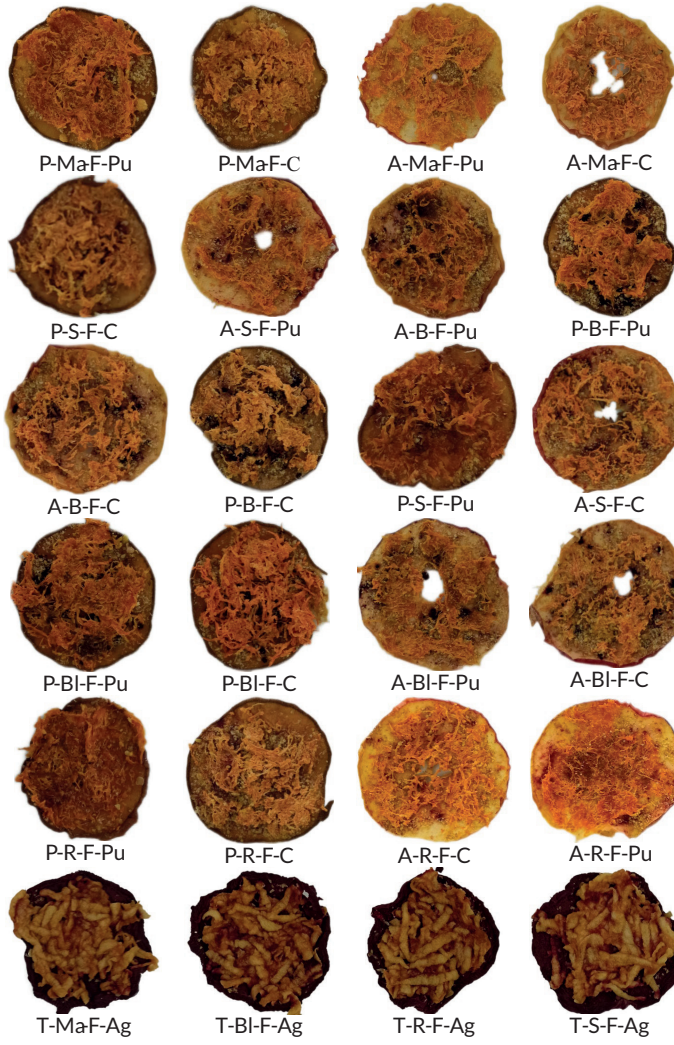

Fig. 5.3 Samples of multilayer fruit and vegetable chips

The surface of multilayer chips from the base layer side was typical of dried vegetable and fruit slices. Due to added layers of crushed flax seeds and grated vegetables or fruits, the surface of multilayer chips was uneven. The appearance of

multilayer chips A-R-F-C (4.86±0.35), P-Ma-F-Pu and A-R-F-Pu (4.71±0.45) was rated the highest. And the appearance of the P-B-F-C composition was rated the lowest (3.43±0.50).

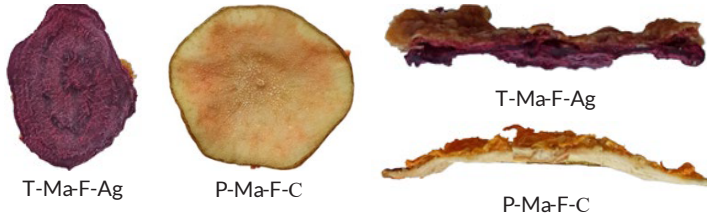

Fig. 5.4 The appearance of the samples from the base layer side and their cross-section

The colour of the multilayer chips was similar to the colour of dried vegetables and fruits, mostly different shades of yellow and brown. Multilayer chips with a pear base layer were darker in colour than chips with an apple base layer. The table beet base of the chips was dark maroon with a light brown apple layer. The addition of freeze-dried plant powders significantly affected the colour of the chips. Bilberry and blueberry powders, which have a burgundy colour, caused the multilayer chips to have unsightly dark spots. Freeze-dried mango powder was not visible on the surface of the multilayer chips because it took on the colour of dried fruits and vegetables after drying. Strawberry and raspberry powders caused dark brown spots on the surface of the chips after drying. Crushed flax seeds, which were brown in colour, was also visible on the surface of the multilayer chips. No plant powders were visible on the beetroot-based chips. Developed chips with a base layer of apple and freeze-dried mango powder received high scores (4.57–4.71) because they had an attractive colour of traditional chips. The P-B-F-C and P-Bl-F-Pu compositions of chips received the lowest score (2.86±0.35).

Multilayer chips tasted like the dried fruits, berries, and vegetables used in the recipe. Developed chips had dried fruit and berry smell. Apple-based chips with blueberry and bilberry powders had a sour taste. Pear-based multilayer chips had a sweet taste. All beet-based chips tasted like table beets. The taste of freeze-dried mango powder was not noticeable in the chips. Instead, strawberry and raspberry powders gave the multilayer chips a pleasant taste and smell of these berries. There was also an aftertaste of flax seeds, dried carrot and pumpkin. Multilayer chips with an apple base layer scored higher than those with a pear base layer.

The A-S-F-Pu composition received the highest score (4.86±0.35) for taste. According to the experts, P-Ma-F-C multilayer chips had the least pleasant

taste (3.71±0.45). Two compositions (A-S-F-C and A-R-F-Pu) received the highest score (5.00±0.00) for smell.

The consistency of all compositions of multilayer chips was crispy and brittle, i. e. similar to traditional chips. This consistency is due to the moisture content of the multilayer chips of 6–8 %. The consistency of the developed chips was rated by experts with high scores of 4.29–4.86. A special feature of multilayer chips is the feeling of crushed flax seeds in the mouth.

Table 5.1 Evaluation of the sensory properties of multilayer chips

Multilayer chips	Appearance	Colour	Taste	Smell	Consistency
P-Ma-F-Pu	4.71±0.45	4.14±0.35	3.86±0.35	4.00±0.00	4.57±0.50
P-Ma-F-C	4.57±0.50	4.00±0.00	3.71±0.45	4.00±0.00	4.43±0.50
A-Ma-F-Pu	4.43±0.50	4.57±0.50	4.14±0.35	4.14±0.35	4.71±0.45
A-Ma-F-C	4.29±0.45	4.57±0.50	4.00±0.00	4.14±0.35	4.71±0.45
P-S-F-C	4.14±0.35	4.14±0.35	4.43±0.50	4.57±0.50	4.29±0.45
A-S-F-Pu	4.29±0.45	4.29±0.45	4.86±0.35	4.57±0.50	4.43±0.50
A-B-F-Pu	3.86±0.35	3.71±0.45	4.00±0.00	4.14±0.35	4.57±0.50
P-B-F-Pu	3.57±0.50	3.57±0.50	4.00±0.00	4.00±0.00	4.43±0.50
A-B-F-C	3.86±0.35	3.57±0.50	4.29±0.45	4.29±0.45	4.43±0.50
P-B-F-C	3.43±0.50	2.86±0.35	3.86±0.35	4.00±0.45	4.57±0.50
P-S-F-Pu	3.86±0.35	3.00±0.00	4.43±0.50	4.86±0.35	4.43±0.50
A-S-F-C	4.14±0.35	3.71±0.45	4.71±0.45	5.00±0.00	4.71±0.45
P-Bl-F-Pu	3.57±0.50	2.86±0.35	4.00±0.00	4.29±0.45	4.43±0.50
P-Bl-F-C	3.71±0.45	3.00±0.35	4.00±0.00	4.29±0.45	4.43±0.50
A-Bl-F-Pu	4.00±0.00	3.86±0.35	4.29±0.45	4.57±0.50	4.86±0.35
A-Bl-F-C	3.71±0.45	3.86±0.35	4.14±0.35	4.57±0.50	4.86±0.35
P-R-F-Pu	4.29±0.45	3.14±0.35	4.29±0.45	4.71±0.45	4.43±0.50
P-R-F-C	4.43±0.50	3.71±0.45	4.29±0.45	4.71±0.45	4.29±0.45
A-R-F-C	4.86±0.35	4.71±0.45	4.57±0.50	4.86±0.35	4.86±0.35
A-R-F-Pu	4.71±0.45	4.57±0.50	4.71±0.45	5.00±0.00	4.86±0.35
T-Ma-F-Ag	3.86±0.35	3.71±0.45	4.14±0.35	4.71±0.45	4.71±0.45
T-Bl-F-Ag	3.86±0.35	3.71±0.45	4.71±0.45	4.71±0.45	4.71±0.45
T-R-F-Ag	3.86±0.35	3.71±0.45	4.71±0.45	4.86±0.35	4.71±0.45
T-S-F-Ag	3.86±0.35	3.71±0.45	4.43±0.50	4.86±0.35	4.71±0.45

In order to generalise the results of the sensory analysis of the developed multilayer chips, the quality index of chips Q was calculated (**Table 5.2**). To calculate the quality index, the weighting coefficients of the sensory properties of chips were determined as follows: appearance – m_1=0.24; colour – m_2=0.15; taste – m_3=0.30; smell – m_4=0.11; consistency – m_5=0.20.

Among the multilayer chips with a pear base layer, the P-S-F-C composition obtained the highest value of the quality index (Q=0.861), and the lowest value – P-B-F-C (Q=0.753). Among the chips with an apple base layer, the A-R-F-Pu composition received the highest value of the quality index (Q=0.950). The T-R-F-Ag composition was rated the highest (Q=0.875) among beet-based chips. The following multilayer chips also obtained a high-quality index: A-S-F-Pu – Q=0.904; A-R-F-C – Q=0.920. Among the apple-based chips, the A-B-F-Pu composition had the lowest quality index (Q=0.810).

Table 5.2 Quality index of multilayer chips

Multilayer chips	Quality index Q	Multilayer chips	Quality index Q
P-Ma-F-Pu	0.853	P-S-F-Pu	0.825
P-Ma-F-C	0.827	A-S-F-C	0.891
A-Ma-F-Pu	0.878	P-Bl-F-Pu	0.769
A-Ma-F-C	0.863	P-Bl-F-C	0.780
P-S-F-C	0.861	A-Bl-F-Pu	0.860
A-S-F-Pu	0.904	A-Bl-F-C	0.837
A-B-F-Pu	0.810	P-R-F-Pu	0.838
P-B-F-Pu	0.784	P-R-F-C	0.857
A-B-F-C	0.821	A-R-F-C	0.920
P-B-F-C	0.753	A-R-F-Pu	0.950
T-Ma-F-Ag	0.837	T-R-F-Ag	0.875
T-Bl-F-Ag	0.871	T-S-F-Ag	0.858

5.5.2 Nutritional value and calorie content of multilayer fruit and vegetable chips

The nutritional value and calorie content of multilayer fruit and vegetable chips are presented in **Table 5.3**. The nutrient content of multilayer chips depended on

their composition. It was found to be in the range of (g 100 g^{-1}): protein – 5.77–9.12; fat – 8.32–8.66; carbohydrates – 37.42–53.92. Beet chips had the highest protein content (8.95–9.12 g 100 g^{-1}). Multilayer chips with grated carrot had a higher protein content than chips with grated pumpkin, when other ingredients were equal. Chips with mango and strawberry powders had lower protein content than those with blueberry, bilberry, and raspberry powders. The addition of freeze-dried blueberry powder and pumpkin to the recipe of multilayer chips resulted in a decrease in the fat content compared to other ingredient combinations. However, the fat content of chips with different combinations of plant-based ingredients varied slightly. The T-R-F-Ag composition had the highest fat content (8.66 g 100 g^{-1}). Flax seeds are a source of protein and fat, so adding it to chips can increase the amount of these nutrients in the finished product. Carbohydrate content decreased in multilayer chips with the addition of freeze-dried blueberry powder compared to other freeze-dried plant powders. Multilayer chips with grated carrot had a higher carbohydrate content than chips with grated pumpkin.

The calorie content of multilayer fruit and vegetable chips varied between 238.9 and 312.0 kcal 100 g^{-1}. Multilayer chips containing grated carrot had more calories than those containing grated pumpkin. The T-R-F-Ag composition had the highest calorie content (312.0 kcal 100 g^{-1}). Chips containing pear, blueberry powder, crushed flax seeds and grated pumpkin had the lowest calories (238.9 kcal 100 g^{-1}).

Table 5.4 shows the mineral content of multilayer chips. The mineral content of the chips varied as follows (mg 100 g^{-1}): iron (Fe) – 1.58–4.51; magnesium (Mg) – 105.34–139.36; calcium (Ca) – 64.57–107.41; potassium (K) – 447.53–769.71. The highest iron content (4.51 mg 100 g^{-1}) was in the A-S-F-C composition. Chips containing apple and carrot had the highest iron content, while samples containing pear and pumpkin had the lowest. The strawberry powder enriched the chips with iron more than the other powders used. The T-S-F-Ag composition had the highest magnesium content (139.36 mg 100 g^{-1}). Compositions of chips containing apple and carrot had higher magnesium content than samples containing combinations of such raw materials: apple-pumpkin, pear-pumpkin, pear-carrot. The addition of raspberry and strawberry powders fortified the chips with magnesium. The A-R-F-C composition had the highest calcium content (107.41 mg 100 g^{-1}). Compositions of multilayer chips containing carrot had a higher calcium content than those containing other ingredients. The highest calcium enrichment of chips was found when raspberry powder was added. The highest potassium content (769.71 mg 100 g^{-1}) was found in the A-R-F-C composition of chips. Samples containing carrot had the highest potassium content. The addition of raspberry powder fortified the chips with potassium more than the addition of other freeze-dried plant powders.

Table 5.3 Nutritional value and calorie content of multilayer chips

Multilayer chips	Protein, g 100 g^{-1}	Fat, g 100 g^{-1}	Carbohydrates, g 100 g^{-1}	Calorie content, kcal 100 g^{-1}
P-Ma-F-Pu	5.77±0.24	8.39±0.14	38.90±0.98	244.4
P-Ma-F-C	7.57±0.31	8.48±0.16	53.42±1.21	306.9
A-Ma-F-Pu	5.77±0.21	8.39±0.16	37.85±0.87	240.5
A-Ma-F-C	7.57±0.26	8.48±0.13	52.37±1.13	302.9
P-S-F-C	7.58±0.26	8.49±0.15	53.37±1.15	306.8
A-S-F-Pu	5.78±0.22	8.40±0.15	39.30±0.96	246.1
A-B-F-Pu	5.92±0.19	8.38±0.18	39.40±0.94	246.8
P-B-F-Pu	5.92±0.21	8.38±0.15	38.95±1.01	245.1
A-B-F-C	7.72±0.30	8.47±0.14	53.92±1.17	309.3
P-B-F-C	7.72±0.29	8.47±0.16	53.47±1.22	307.6
P-S-F-Pu	5.78±0.18	8.40±0.16	38.85±0.95	244.4
A-S-F-C	7.58±0.24	8.49±0.13	53.82±1.14	308.5
P-Bl-F-Pu	5.94±0.20	8.32±0.10	37.42±1.03	238.9
P-Bl-F-C	7.74±0.27	8.41±0.16	51.94±1.17	301.4
A-Bl-F-Pu	5.94±0.18	8.32±0.12	37.87±1.00	240.6
A-Bl-F-C	7.74±0.25	8.41±0.15	52.39±1.19	303.0
P-R-F-Pu	5.93±0.19	8.49±0.15	38.58±0.92	244.8
P-R-F-C	7.73±0.25	8.58±0.16	53.10±1.15	307.3
A-R-F-C	7.73±0.28	8.58±0.14	53.55±1.18	309.0
A-R-F-Pu	5.93±0.17	8.49±0.15	39.03±1.03	246.5
T-Ma-F-Ag	8.95±0.11	8.55±0.12	53.04±1.06	311.6
T-Bl-F-Ag	9.12±0.14	8.48±0.16	51.56±1.12	306.1
T-R-F-Ag	9.11±0.12	8.66±0.09	52.72±1.00	312.0
T-S-F-Ag	8.96±0.07	8.57±0.06	52.99±1.08	311.6

Table 5.4 Mineral content of multilayer chips

Multilayer chips	Mineral content, mg 100 g^{-1}			
	Fe	Mg	Ca	K
P-Ma-F-Pu	1.69	108.09	64.57	468.58
P-Ma-F-C	2.41	120.09	85.78	697.48
A-Ma-F-Pu	3.45	114.89	82.39	521.09
A-Ma-F-C	4.17	126.89	103.60	750.00
P-S-F-C	2.76	120.70	100.94	709.06
A-S-F-Pu	3.79	115.49	84.23	532.67
A-B-F-Pu	3.49	113.46	82.33	511.26
P-B-F-Pu	1.73	106.66	77.83	458.75
A-B-F-C	4.21	125.46	103.54	740.16
P-B-F-C	2.45	118.66	99.04	687.65
P-S-F-Pu	2.04	108.70	100.94	480.16
A-S-F-C	4.51	127.49	105.44	761.57
P-Bl-F-Pu	1.58	105.34	74.31	447.53
P-Bl-F-C	2.30	117.34	95.52	676.43
A-Bl-F-Pu	3.33	112.14	78.81	500.04
A-Bl-F-C	4.05	124.14	100.02	728.94
P-R-F-Pu	1.73	110.92	81.70	488.30
P-R-F-C	2.45	122.92	102.91	717.20
A-R-F-C	4.21	129.71	107.41	769.71
A-R-F-Pu	3.49	117.71	86.20	540.81
T-Ma-F-Ag	3.19	117.39	81.64	496.72
T-Bl-F-Ag	3.07	114.64	78.06	475.67
T-R-F-Ag	3.23	136.00	85.45	516.44
T-S-F-Ag	3.53	139.36	83.48	508.30

5.6 Characteristic of multilayer glazed fruit and vegetable chips

5.6.1 Sensory properties of multilayer glazed fruit and vegetable chips

The multilayer glazed fruit and vegetable chips are shown in **Fig. 5.5** (samples of glazed chips are marked as follows: A – solid apple slice; T – solid table beet slice; Z – solid zucchini slice; F – crushed flax seeds; Ag – grated apple; C – grated carrot; D – dark chocolate; M – milk chocolate; W – white chocolate; Cu – currant powder). **Fig. 5.6** shows the appearance of the A-F-C-D-Cu sample from the base layer side and its cross-section. The base layer of the multilayer glazed chips was a solid slice of apple, table beet or zucchini. The apple, table beet and zucchini slices were breaded on one side with crushed flax seeds. Grated apple and carrot were used to form the layer over crushed flax seeds. Different types of chocolate (dark, milk, and white) and freeze-dried currant powder were used to prepare the glaze for the multilayer chips.

The results of the expert evaluation of the sensory properties of multilayer glazed chips are presented in **Table 5.5**. **Table 5.6** shows the results of determining the colour of multilayer glazed chips using the RGB additive colour model.

The shape and size of the multilayer chocolate-glazed chips depended on the shape and size of the fruits and vegetables used for the base layer of the chips. On the side of the base layer, the multilayer glazed chips had a smooth, wavy surface covered by the chocolate glaze. On the opposite side, the glazed chips had a bumpy surface that was the result of applying a glaze to a layer of grated fruit or vegetable. Some samples of chips had cracks in the glaze (e. g. A-F-C-D and A-F-Ag-D samples). On the side of the grated fruit and vegetable layer, small localized areas of the chips were not completely covered by the glaze. To eliminate these defects, it is necessary to grate the fruits and vegetables finer for the top layer of multilayer chips and also to make this layer thinner. The inner fruit and vegetable layers of all samples of glazed chips were not crisp and brittle. The glaze crumbled when the chips were cut and became sticky where the chips were held by the fingers [40].

The appearance, colour, taste and smell of the multilayer glazed chips depended on the combination of ingredients: vegetables, fruits, plant powders and chocolate. The sensory properties of the multilayer chips with glaze containing white chocolate and freeze-dried currant powder were rated higher (appearance – 3.29–4.71; colour – 3.29–4.71; taste – 4.29–4.71; smell – 4.00–4.71) than those of the chips with glaze containing white chocolate only (appearance – 3.00–3.29; colour – 3.00–3.71; taste – 3.29–4.29; smell – 4.00–4.71). The addition of currant powder to the white chocolate glaze did not significantly affect the smell rating of the chips. Glaze with white chocolate and currant powder made the appearance of the chips more attractive.

Fig. 5.5 Samples of multilayer glazed fruit and vegetable chips [40]

A-F-C-D-Cu

A-F-C-D-Cu

Fig. 5.6 The appearance of the A-F-C-D-Cu sample from the base layer side and its cross-section

The berry powder gave the white chocolate glaze a sweet-sour flavor that harmonized with the flavor of the dried vegetables and fruits. The sensory properties of multilayer glazed chips with an apple had higher scores than the sensory properties of the chips with zucchini. The consistency of the white chocolate glazed chips ranged from 1.71 to 3.00 points. Such low scores are due to the fact that the glazed multilayer chips did not have a crisp consistency.

Milk chocolate glazed chips had the following sensory property scores: appearance – 3.71–4.00; colour – 3.29–4.00; taste – 3.29–4.71; smell – 4.00–4.29; consistency – 1.29–2.00. The sensory properties of the multilayer glazed chips were improved by adding currant powder to the milk chocolate glaze as follows: appearance – 4.29–5.00; colour – 4.00–4.71; taste – 3.71–5.00; smell – 4.00–4.71. The consistency scores of the chips continued to be low (1.29–3.00). Milk chocolate glazed multilayer chips were light brown, while those glazed with milk chocolate glaze with currant powder were dark brown. Milk chocolate glazed chips had a sweet chocolate taste with a hint of the vegetable or fruit used. And milk chocolate glazed chips with currant powder had a sweet and sour taste, but the chocolate taste was dominant. All samples of the milk chocolate glazed chips had a slight chocolate flavor.

The appearance of the dark chocolate glazed chips with currant powder was rated from 4.71 to 5.00 points, and the appearance of the dark chocolate glazed chips was rated from 4.29 to 5.00 points. The colour of chips glazed with dark chocolate was dark brown, it was rated from 4.29 to 5.00 points. When currant powder was added, the colour of the chips became darker. The dark chocolate glazed chips had a bitter taste of dark chocolate. Adding currant powder to the glaze gave the chips a sour taste. The glazed beet chips had a beet aftertaste. The taste score of dark chocolate glazed chips ranged from 3.29 to 5.00. In addition, chips containing an apple had the highest score 5.0 ± 0.00. Adding freeze-dried currant powder to the dark chocolate glaze did not affect the smell of the chips, they all had a light chocolate smell. The smell of chips with dark chocolate glaze was estimated at 3.71–4.71 points. The consistency of the dark chocolate-covered chips was estimated at 1.71–3.00 points.

Table 5.5 Evaluation of the sensory properties of multilayer glazed chips [40]

Multilayer glazed chips	Appearance	Colour	Taste	Smell	Consistency
Z-F-Ag-W	3.29±0.45	3.29±0.45	4.00±0.00	4.00±0.00	2.00±0.00
Z-F-Ag-M	4.00±0.00	4.00±0.00	4.00±0.00	4.00±0.00	2.00±0.00
Z-F-Ag-D	4.71±0.45	4.71±0.45	3.71±0.45	4.00±0.00	2.29±0.45
Z-F-Ag-W-Cu	4.29±0.45	4.29±0.45	4.71±0.45	4.00±0.00	2.00±0.00
Z-F-Ag-M-Cu	4.71±0.45	4.71±0.45	4.71±0.45	4.00±0.00	2.00±0.00
Z-F-Ag-D-Cu	4.71±0.45	4.71±0.45	4.71±0.45	4.00±0.00	2.29±0.45
Z-F-C-W	3.29±0.45	3.71±0.45	3.29±0.45	4.00±0.00	2.00±0.00
Z-F-C-M	3.71±0.45	3.29±0.45	3.29±0.45	4.00±0.00	2.00±0.00
Z-F-C-D	4.29±0.45	4.29±0.45	3.29±0.45	3.71±0.45	2.29±0.45
Z-F-C-W-Cu	4.29±0.45	4.29±0.45	4.29±0.45	4.29±0.45	2.00±0.00
Z-F-C-M-Cu	4.29±0.45	4.00±0.00	3.71±0.45	4.00±0.00	2.00±0.00
Z-F-C-D-Cu	4.71±0.45	4.71±0.45	4.29±0.45	3.71±0.45	2.29±0.45
A-F-C-W	3.00±0.00	3.29±0.45	4.29±0.45	4.29±0.45	2.00±0.00
A-F-C-M	3.71±0.45	3.29±0.45	4.29±0.45	4.29±0.45	1.71±0.45
A-F-C-D	5.00±0.00	5.00±0.00	4.00±0.00	4.71±0.45	2.29±0.45
A-F-C-W-Cu	4.71±0.45	4.71±0.45	4.71±0.45	4.71±0.45	2.00±0.00
A-F-C-M-Cu	4.71±0.45	4.71±0.45	5.00±0.00	4.29±0.45	1.71±0.45
A-F-C-D-Cu	5.00±0.00	5.00±0.00	3.71±0.45	4.71±0.45	2.29±0.45
A-F-Ag-W	3.29±0.45	3.00±0.00	4.29±0.45	4.71±0.45	1.71±0.45
A-F-Ag-M	4.00±0.00	3.71±0.45	4.71±0.45	4.29±0.45	1.29±0.45
A-F-Ag-D	5.00±0.00	5.00±0.00	4.71±0.45	4.71±0.45	2.00±0.00
A-F-Ag-W-Cu	4.00±0.00	4.29±0.45	4.71±0.45	4.71±0.45	1.71±0.45
A-F-Ag-M-Cu	5.00±0.00	4.71±0.45	5.00±0.00	4.71±0.45	1.29±0.45
A-F-Ag-D-Cu	5.00±0.00	5.00±0.00	5.00±0.00	4.71±0.45	1.71±0.45
T-F-Ag-D	5.00±0.00	5.00±0.00	4.00±0.00	4.71±0.45	3.00±0.00
T-F-Ag-D-Cu	5.00±0.00	4.71±0.45	4.29±0.45	4.71±0.45	3.00±0.00
T-F-Ag-W-Cu	3.29±0.45	3.29±0.45	4.29±0.45	4.71±0.45	3.00±0.00
T-F-Ag-M-Cu	4.71±0.45	4.71±0.45	4.29±0.45	4.71±0.45	3.00±0.00

Table 5.6 Colour of multilayer glazed chips

Multilayer glazed chips	RGB colours	Multilayer glazed chips	RGB colours
Z-F-Ag-W	133, 78, 43	A-F-C-W	152, 124, 112* 181, 81, 31**
Z-F-Ag-M	89, 50, 30	A-F-C-M	86, 46, 42* 107, 32, 15**
Z-F-Ag-D	36, 14, 3	A-F-C-D	54, 34, 30
Z-F-Ag-W-Cu	68, 37, 39	A-F-C-W-Cu	120, 86, 80* 181, 81, 31**
Z-F-Ag-M-Cu	47, 23, 24	A-F-C-M-Cu	77, 35, 25
Z-F-Ag-D-Cu	33, 25, 27	A-F-C-D-Cu	56, 33, 27
Z-F-C-W	156, 112, 79* 181, 81, 31**	A-F-Ag-W	178, 142, 94
Z-F-C-M	68, 29, 18* 107, 41, 31**	A-F-Ag-M	101, 46, 29
Z-F-C-D	43, 32, 33	A-F-Ag-D	48, 27, 23
Z-F-C-W-Cu	121, 87, 82* 181, 81, 31**	A-F-Ag-W-Cu	102, 73, 67
Z-F-C-M-Cu	50, 25, 20	A-F-Ag-M-Cu	77, 36, 27
Z-F-C-D-Cu	27, 19, 24	A-F-Ag-D-Cu	33, 13, 13
T-F-Ag-D	64, 39, 33	T-F-Ag-W-Cu	176, 137, 120
T-F-Ag-D-Cu	64, 39, 35	T-F-Ag-M-Cu	87, 42, 25

*Note: *main colour; **colour of the carrot visible under the glaze*

The weighting coefficients of the sensory properties of multilayer chocolate glazed chips, which were used to calculate the quality index, were determined as follows [40]: appearance – $m_1=0.25$; colour – $m_2=0.15$; taste – $m_3=0.33$; smell – $m_4=0.11$; consistency – $m_5=0.16$. The calculated quality index of the multilayer chocolate glazed chips is shown in **Table 5.7**.

Compositions of multilayer chips containing chocolate glaze with freeze-dried currant powder had a higher value of the quality index than chips where the glaze did not contain currant powder. The exception was the A-F-C-D-Cu composition with a quality index $Q=0.822$, since the A-F-C-D composition had a lower quality index $Q=0.842$. The A-F-C-W-Cu composition had the highest quality index value ($Q=0.854$) among the chips with white chocolate. The quality index of the milk

chocolate-covered chips ranged from 0.654 to 0.866, with the A-F-Ag-M-Cu composition (Q=0.866) having the highest value (Q=0.866). The quality index of the multilayer chips with dark chocolate varied within 0.716–0.888. The A-F-Ag-D-Cu composition had the highest value of the quality index Q=0.888. Therefore, the dark chocolate glazed chips had the highest quality indices.

Table 5.7 Quality index of multilayer glazed chips [40]

Multilayer glazed chips	Quality index *Q*	Multilayer glazed chips	Quality index *Q*
Z-F-Ag-W	0.700	A-F-C-W	0.692
Z-F-Ag-M	0.736	A-F-C-M	0.716
Z-F-Ag-D	0.782	A-F-C-D	0.842
Z-F-Ag-W-Cu	0.806	A-F-C-W-Cu	0.854
Z-F-Ag-M-Cu	0.838	A-F-C-M-Cu	0.856
Z-F-Ag-D-Cu	0.848	A-F-C-D-Cu	0.822
Z-F-C-W	0.646	A-F-Ag-W	0.696
Z-F-C-M	0.654	A-F-Ag-M	0.758
Z-F-C-D	0.716	A-F-Ag-D	0.878
Z-F-C-W-Cu	0.786	A-F-Ag-W-Cu	0.798
Z-F-C-M-Cu	0.732	A-F-Ag-M-Cu	0.866
Z-F-C-D-Cu	0.814	A-F-Ag-D-Cu	0.888
T-F-Ag-D	0.864	T-F-Ag-W-Cu	0.746
T-F-Ag-D-Cu	0.874	T-F-Ag-M-Cu	0.860

5.6.2 Nutritional value and calorie content of multilayer glazed fruit and vegetable chips

The nutritional value and calorie content of the multilayer chocolate glazed chips are presented in **Table 5.8**. The nutritional content of the developed compositions of chocolate-covered chips is as follows (g 100 g^{-1}): protein – 8.02–11.94; fat – 15.09–18.02; carbohydrates – 47.48–58.23. The effect of adding freeze-dried currant powder to the glaze of different types of chocolate on the protein, fat and carbohydrate content of multilayer glazed chips is statistically insignificant. This is due to the small amount of currant powder in the chocolate glaze.

Table 5.8 Nutritional value and calorie content of multilayer glazed chips [40]

Multilayer glazed chips	Protein, g 100 g^{-1}	Fat, g 100 g^{-1}	Carbohydrates, g 100 g^{-1}	Calorie content, kcal 100 g^{-1}
Z-F-Ag-W	10.40±0.37	17.92±0.42	54.32±1.17	406.0
Z-F-Ag-M	9.89±0.34	16.63±0.38	55.49±1.02	397.6
Z-F-Ag-D	10.03±0.29	17.41±0.51	53.67±1.10	398.3
Z-F-Ag-W-Cu	10.44±0.31	17.93±0.44	54.50±1.09	406.9
Z-F-Ag-M-Cu	9.92±0.24	16.72±0.36	55.92±0.98	398.0
Z-F-Ag-D-Cu	10.03±0.37	17.40±0.38	53.83±1.15	398.8
Z-F-C-W	11.91±0.36	18.02±0.40	48.22±1.07	390.1
Z-F-C-M	11.39±0.42	16.84±0.39	49.32±1.09	381.2
Z-F-C-D	11.52±0.40	17.63±0.39	47.48±1.16	382.0
Z-F-C-W-Cu	11.94±0.33	18.01±0.33	48.34±1.11	390.5
Z-F-C-M-Cu	11.41±0.28	16.82±0.34	49.40±1.14	381.7
Z-F-C-D-Cu	11.52±0.37	17.60±0.42	47.62±1.00	382.5
A-F-C-W	9.92±0.32	16.72±0.45	50.82±1.13	380.8
A-F-C-M	9.39±0.35	15.49±0.36	51.88±1.02	372.0
A-F-C-D	9.51±0.33	16.29±0.18	50.21±1.10	372.8
A-F-C-W-Cu	9.91±0.38	16.72±0.25	50.93±1.17	381.3
A-F-C-M-Cu	9.40±0.40	15.53±0.18	52.03±1.08	372.5
A-F-C-D-Cu	9.52±0.37	16.29±0.30	50.32±1.08	373.2
A-F-Ag-W	8.52±0.36	16.58±0.33	57.04±1.11	397.2
A-F-Ag-M	8.03±0.38	15.40±0.31	58.12±1.19	388.3
A-F-Ag-D	8.14±0.27	16.23±0.35	56.41±1.15	389.1
A-F-Ag-W-Cu	8.52±0.35	16.59±0.29	57.10±1.14	397.6
A-F-Ag-M-Cu	8.02±0.31	15.40±0.36	58.23±1.01	388.8
A-F-Ag-D-Cu	8.14±0.26	16.21±0.19	56.52±1.07	389.5
T-F-Ag-D	8.33±0.26	16.12±0.22	50.18±1.02	366.6
T-F-Ag-D-Cu	8.33±0.18	16.11±0.24	51.01±1.08	369.6
T-F-Ag-W-Cu	8.40±0.21	15.12±0.18	52.49±1.19	366.5
T-F-Ag-M-Cu	8.27±0.17	15.09±0.11	52.64±1.21	366.4

The protein content of multilayer chips covered with different types of chocolate varies as follows (g 100 g^{-1}):

– covered with white chocolate – 8.40–11.94;
– covered with milk chocolate – 8.02–11.41;
– covered with dark chocolate – 8.14–11.52.

Chips containing apple and table beet had lower protein content than those containing zucchini and carrots.

Multilayer chips glazed with milk chocolate had the lowest fat content (15.09–16.84 g 100 g^{-1}). The fat content of chips glazed with white and dark chocolate was 15.12–18.02 g 100 g^{-1} and 16.11–17.63 g 100 g^{-1}, respectively. Regardless of the type of chocolate used for the glaze, the fat content of the zucchini and carrot chips was higher.

Chips glazed with dark chocolate had the lowest carbohydrate content 47.48–56.52. The carbohydrate content of chips glazed with white and milk chocolate was 48.22–57.10 and 49.32–58.23, respectively. The highest carbohydrate content was found in multilayer chips in which the plant raw material of the base and the grated layer was apple.

The calorie content of chocolate-glazed chips ranged from 366.4 to 406.9 kcal 100 g^{-1}. Chips glazed with white chocolate had more calories than those glazed with milk and dark chocolate.

The mineral content of multilayer glazed chips is presented in **Table 5.9**, which shows the effect of the type of chocolate on the mineral content of the chips. The mineral content of the glazed chips varied as follows (mg 100 g^{-1}):

– iron (Fe) – 2.60–5.10;
– magnesium (Mg) – 92.07–145.88;
– calcium (Ca) – 71.22–212.25;
– potassium (K) – 457.8–1228.0.

Multilayer chips glazed with dark chocolate had a higher iron content than those glazed with white and milk chocolate. The iron content of the chips was also increased by adding currant powder to the chocolate glaze. The highest iron content (5.10 mg 100 g^{-1}) was found in the A-F-Ag-D-Cu composition. The highest magnesium levels were also found in compositions glazed with dark chocolate. Adding currant powder to the glaze increased the magnesium content of the chips. The Z-F-C-D-Cu composition had the highest magnesium content (145.88 mg 100 g^{-1}). Milk glazed multilayer chips with currant powder had the highest calcium and potassium levels. Multilayer chips glazed with dark chocolate had the lowest calcium content. The lowest potassium levels were found in chips with white chocolate glaze.

Table 5.9 Mineral content of multilayer glazed chips

Multilayer glazed chips	Mineral content, mg 100 g^{-1}			
	Fe	Mg	Ca	K
Z-F-Ag-W	3.20	106.83	151.50	1075.0
Z-F-Ag-M	3.58	123.63	197.40	1127.0
Z-F-Ag-D	4.81	143.13	105.30	1098.0
Z-F-Ag-W-Cu	3.39	109.57	151.99	1087.0
Z-F-Ag-M-Cu	3.74	125.25	194.83	1137.0
Z-F-Ag-D-Cu	4.89	143.45	108.87	1109.0
Z-F-C-W	2.77	109.25	166.35	1166.0
Z-F-C-M	3.15	126.05	212.25	1219.0
Z-F-C-D	4.38	145.55	120.15	1189.0
Z-F-C-W-Cu	2.96	112.00	166.84	1179.0
Z-F-C-M-Cu	3.31	127.68	209.68	1228.0
Z-F-C-D-Cu	4.46	145.88	123.72	1201.0
A-F-C-W	2.98	96.14	135.03	632.3
A-F-C-M	3.36	112.94	180.93	685.1
A-F-C-D	4.59	132.44	88.83	655.4
A-F-C-W-Cu	3.17	98.89	135.52	645.0
A-F-C-M-Cu	3.52	114.57	178.36	694.3
A-F-C-D-Cu	4.67	132.77	92.40	666.7
A-F-Ag-W	3.41	93.72	120.18	540.6
A-F-Ag-M	3.79	110.52	166.08	593.4
A-F-Ag-D	5.00	130.02	73.98	563.7
A-F-Ag-W-Cu	3.60	96.46	120.67	553.3
A-F-Ag-M-Cu	3.95	112.14	163.51	602.6
A-F-Ag-D-Cu	5.10	130.34	77.55	574.9
T-F-Ag-D	4.02	125.63	71.22	468.2
T-F-Ag-D-Cu	4.10	125.95	74.79	479.4
T-F-Ag-W-Cu	2.60	92.07	117.91	457.8
T-F-Ag-M-Cu	2.96	107.75	160.75	507.1

Conclusions

Fruits, vegetables, and berries are seasonal products that spoil quickly and lose nutrients without proper storage conditions. Long-term storage of fruits, vegetables and berries requires the creation of special conditions that maintain recommended air temperature and air humidity regimes. Storage is an energy-intensive process and requires large warehouses. Therefore, it is advisable to process fruits, vegetables and berries directly at the farms where they are grown. The processing of these plant raw materials, in particular the production of chips from them, will allow agricultural producers not to lose the harvested crop, to refuse significant costs for its storage and to obtain additional profits. However, the production of chips requires technological equipment and production buildings for its installation, as well as qualified personnel.

Dried fruit and vegetable chips are positioned in the market as a healthy food. They can be a healthy snack between main meals. Their consumption allows the human body to obtain the necessary nutrients, especially vitamins, macro- and microelements. Chips made of plant raw materials can have a positive effect on the metabolism in the human body, prevent excessive food consumption and provide a balanced diet.

The results of the study can be summarized as follows:

1. For the production of "healthy" chips it is important to choose an effective technology. For their production it is recommended to use hot air drying at the temperature of the drying agent up to 80 °C. At this drying temperature, the nutrients contained in fresh fruits and vegetables can be preserved without significant losses in the finished product. In addition, in order to reduce the loss of nutrients during the production of chips, as well as to preserve the taste, smell and colour of the plant raw materials in the finished product, it is advisable to blanch the plant raw materials for a short time.

2. The processing of fruits, vegetables and berries into freeze-dried powders is a promising technology. Freeze-dried plant powders, especially raspberry, currant and strawberry, can be used in various combinations as an ingredient in multilayer chips to fortify them with minerals, as well as to diversify flavors.

3. Flax seeds are another innovative ingredient for chips. It is a source of useful substances for the human body. The combination of flax seeds with vegetables and fruits in one product (chips) makes it possible to balance the nutritional content.

4. Glazing multilayer chips with different types of chocolate increases the calorie content of snacks. The dark chocolate glaze fortifies the multilayer chips with iron and magnesium, and the milk chocolate glaze fortifies the chips with calcium and potassium. These chips can be recommended for children because they contain fruits and vegetables. At the same time, it is important that children consume these snacks in the recommended amounts.

5. Using the developed technology, it is possible to produce an innovative product (multilayer chips or chocolate-glazed multilayer chips) with original taste properties and nutritional composition. The possibility of combining different types of plant raw materials (vegetables, fruits, berries, flax seeds, etc.) in one product allows producers to obtain a wide range of multilayer chips with taste properties that satisfy the preferences of different categories of consumers. The combination of plant raw materials also makes it possible to balance the nutritional content of the chips and obtain a functional product for specific target groups of consumers.

6. According to the results of sensory analysis of chips with different combinations of plant raw materials and determination of the quality index of chips, the following multilayer chips are recommended for production: A-S-F-Pu, A-R-F-C, A-R-F-Pu, T-R-F-Ag. The nutritional value and the calorie content of these chips are in the following range: protein – 5.78–9.11 g 100 g^{-1}; fat – 8.40–8.66 g 100 g^{-1}; carbohydrates – 39.03–53.55 g 100 g^{-1}; calorie content – 246.1–312.0 kcal 100 g^{-1}. The following multilayer chocolate-glazed chips are also recommended for production: T-F-Ag-D-Cu, A-F-Ag-D, A-F-Ag-D-Cu. The nutritional value and the calorie content of these chips are in the following range: protein – 8.14–8.33 g 100 g^{-1}; fat – 16.11–16.23 g 100 g^{-1}; carbohydrates – 51.01–56.52 g 100 g^{-1}; calorie content – 369.6–389.5 kcal 100 g^{-1}.

Further research to determine the physicochemical and sensory properties of multilayer chips with different combinations of plant raw materials such as fresh vegetables, fruits, berries, seeds, freeze-dried plant powders, etc. is relevant.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 6

Improving the quality of dairy sauces by using condensed low-lactose milk whey

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Abstract

For optimal functioning of all organs and systems in the human body, nutrition must be complete and balanced. This is achieved by improving recipes and production technologies of existing food products to preserve their nutritional properties or provide them with new properties. In the presence of associated diseases, especially food allergies, malabsorption or even intolerance to certain food substances, the existing range of food products should be expanded by developing technologies for special nutrition. Mayonnaise products, popular among consumers but not highly biologically valuable or balanced, cannot be included in the diet of individuals allergic to egg products. There have been efforts to replace egg ingredients in mayonnaise with plant-based proteins, but whey proteins in mayonnaise products have not received enough attention. Although secondary dairy raw material – milk whey- is a valuable and cost-effective resource that must be processed, searching for its applications is ongoing. Additionally, mayonnaise products based on whey can not only expand the range of sauces for people allergic to eggs but also serve as a source of animal proteins for lactose-intolerant individuals after lactose removal. This new direction of its use is crucial because previous studies have shown that excluding lactose-containing foods from the diet or partially restricting them does not improve human health. This issue can be addressed using low-lactose protein-carbohydrate dairy raw materials – processed milk whey.

This chapter of the monograph presents research results on the possibility of using fermented mashed pumpkin pulp (FMPP) with a high content of pectin and condensed in vacuo low lactose milk whey (CLLW) in emulsion sauces similar to mayonnaise. Rational oil emulsification parameters have been established, and the characteristics of model samples using FMPP and CLLW in different ratios have been studied. The quality of sauces with an emulsified oil volume of 60 % has been evaluated.

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To establish the rational ratio of main components in the semi-finished product, the rheological properties of model systems have been studied, including their influence on the formation of structuring indicators, such as emulsifying properties. The possibility of using a protein-carbohydrate semi-finished product (SFLLW) based on CLLW and FMPP as a base for emulsion-type sauces like mayonnaise has been demonstrated.

Keywords

Sauce, emulsification, mayonnaise, egg-free sauce, milk whey, fermented mashed pumpkin pulp with a high content of pectin, condensed in vacuo low lactose milk whey, model of the system, lactose intolerance, lactose malabsorption.

6.1 Introduction

Nutrition is one of the most important factors in human life, directly influencing health, productivity, and physical and mental development. For optimal functioning of all organs and systems in the body, nutrition must be complete and balanced.

The issue of rational nutrition among the population holds significant social importance. It plays a crucial role in ensuring the quality and longevity of human life and their health. In Ukraine, the most significant disruptions in the food system include excessive consumption of animal fats and carbohydrates, alongside a deficit of complete proteins of animal origin, polyunsaturated fatty acids, micronutrients, vitamins, and dietary fibers. Therefore, scientists are tasked with creating a range of new products with functional purposes that improve the nutritional status of individuals.

Global trends in nutrition are associated with creating an assortment of functional products that contribute to strengthening public health and reducing the risk of nutrition-related diseases. This task is addressed by including functional ingredients in food products, positively affecting one or several physiological functions of the human body. The creation of functional food products is based on modifying traditional (classical) technologies, allowing for incorporating beneficial ingredients into the finished product within the physiological norms of their consumption (10–50 % of the average daily requirement).

At the same time, the body may find it difficult to absorb nutrients in certain diseases. A common barrier to the complete or partial absorption of certain groups of nutrients is food allergy, intolerance, malabsorption or sensitivity to it. A food allergy happens when the immune system overreacts to a specific protein. Unlike food allergies, food intolerances do not involve the immune system but are missing the enzymes that break down nutrients. The lighter form of intolerance is malabsorption,

when the concentration of enzymes isn't enough to break the nutrient completely. Non-disease sensitivity is a new syndrome of intolerance. Free from this specific nutrient, the diet leads to a complete regression of symptoms. Symptoms can range from mild (rashes, gasses, hives, swelling, itching, etc.) to severe (trouble breathing, loss of consciousness, etc.). More than 170 foods have been reported to cause allergic reactions. The major food allergens are milk because of the lactose as a carbohydrate and egg because of the complex of proteins. Therefore, there is a demand for traditional products in which ingredients that may cause a negative reaction in the body are replaced. One type of such product is sauces. The main sauces and their derivatives mainly contain products that can cause such reactions: milk, eggs, nuts, etc. Therefore, considering the prospects and directions for improving sauce production for special diets is worth considering.

Overall, the global market for food and beverage products aimed at improving health and overall well-being continues to grow at an average rate of 8 %. The number of people consuming functional food products and dietary supplements is constantly increasing.

The international market for sauce products is diverse. However, all products in this category have the same significance, namely as a flavor enhancement for dishes. In this market, the success of launching new products depends on continuously monitoring consumer preferences and analyzing competitive products.

The global mayonnaise market demonstrates steady growth rates, with a projected production increase of approximately 4 % over the next five years [1].

According to data from the State Statistics Service of Ukraine, the Ukrainian Customs Service, and the company "Pro-Consulting", the competition level in the Ukraine sauce market is high, primarily from domestic manufacturers. Mayonnaise production holds the largest market share, accounting for 57 % of the market structure [2].

Mayonnaise is a popular condiment known for its creamy texture and tangy flavor. It is typically produced from a blend of oil, vinegar or lemon juice, egg yolks, and seasonings. The mixture is emulsified to create a smooth and stable sauce. Emulsified fat-containing products play a significant role in nutrition because when fats are consumed, the human body absorbs them only after they are converted into an emulsified state.

It is widely employed as a spread for sandwiches, burgers, and wraps and serves as a base for various dressings and sauces. Its versatility has made it a staple in culinary applications in home kitchens and the commercial food industry. Additionally, it is known for enhancing the taste and mouthfeel of dishes, contributing a rich and satisfying element. Nowadays, it is incorporated into dips and marinades due to its creamy nature across the globe.

The growing food service industry primarily drives the market. In addition, the increasing number of products for convenient and easy meal alternatives, including wraps, salads, and sandwiches, is influencing the market growth. Also, the growing health awareness among consumers, the rising product demand in global culinary options, and the rising disposable incomes are augmenting the market growth. Moreover, introducing health-conscious product variations, including eggless, gluten-free, lactose-free, low-fat, vegan, and vegetarian mayoresses offerings, represents another major growth-inducing factor. Besides this, the shift in consumer lifestyles and the widespread product integration within the food and beverage sector are propelling the market growth. The convenience of procuring products from various retail outlets contributes to market growth. Furthermore, the growing recognition of mayonnaise's nutritional value and versatility creates a positive market outlook. This chapter explores the problems of improving the quality of sauces.

In Ukraine, the production of mayonnaise and mayonnaise-based sauces is regulated by the State Standard of Ukraine 4487:2015, "Mayonnaises and Mayonnaise Sauces. General Technical Conditions". According to section 3.1 of DSTU 4487:2015, mayonnaise is a finely dispersed homogeneous emulsified product with a fat content of not less than 50 %, made from oil, water, egg products, with or without the addition of processed milk products, food additives, and other food ingredients (according to the recipe). Furthermore, according to section 5.4.4 of DSTU 4487:2015, mayonnaise produced under the traditional name "Provansal" must have a fat content of 67 % and an egg product content, including fermented ones, calculated on dry egg yolk of not less than 1.5 %. However, despite their functionality, eggless recipes in industrial production can only be called "a-la mayonnaise", indicating the imperfection and non-inclusivity of Ukrainian legislation. Nevertheless, the existing demand for such products must be met.

First and foremost, excluding egg raw materials from mayonnaise formulation meets the needs of individuals with egg allergies, which affects approximately 1 in 10 adults [3], as well as vegetarians [4].

In their work, Nopparat Prabsangob and Sunsanee Udomrati used acid-modified pea protein isolate and okara cellulose crystal as a co-emulsifier to improve the physicochemical stability of fat-reduced eggless mayonnaise [5]. However, the resulting product had a drawback of a gelatinous consistency and a specific aroma. Miray Büyük, Ada Ata, and Ahmet Yemenicioğlu proposed using aquafaba as a source of mainly water-soluble proteins and carbohydrates, used in combination with citrus pectin and grape seed extract [6] as a co-emulsifier. The major benefit of this technology is related to the reduction of emulsion droplet size, but it still has short-term storage, high risks of lost emulsion and additionally specific organoleptic characteristics.

Another work of innovative technology for developing egg-free mayonnaise was shown, which uses β-carotene and soy-protein binding but has an inappropriate intensive yellow colour [7]. Another obvious disadvantage of this technology is the use of soy proteins since soy is an allergen. However, there are relatively few studies dedicated to using whey proteins for preparing mayonnaise recipes, and all of them are focused on creating recipes for low-fat sauces. The majority of studies also involve the use of dried demineralized whey. However, no studies have been conducted regarding using an intermediate product of its production – condensed whey – including partial demineralization of about 40 % instead of 90 %. An essential point in this case is the necessity of prior lactose removal to prevent crystallization and make this product accessible to individuals with lactose intolerance and malabsorption. This is particularly important since the percentage of such individuals among the populations of Asian and African countries is 90 %, Southern Europe – 70 %, Australia, Northern Europe, and North America – up to 17 %. In Central Europe, it's 30 %; in Southern Europe – 70 %; and in Ukraine, 16 % of the population has been officially diagnosed and confirmed by laboratory tests with malabsorption, with many undiagnosed cases additionally [8]. Including low-lactose food products based on hydrolyzed protein-carbohydrate milk raw materials (PCM) in production will allow the development of a product suitable for consumption by a wide range of consumers.

Acid whey is cheap and a lot in sizes souse, the potential of which in Ukraine is not fully realized for food purposes. As of the first half of 2020, 735 thousand tons of whey were produced, with only 30.4 thousand tons subject to processing, while the rest was discarded as waste [9]. Therefore, the priority issue becomes the creation of technologies for low-lactose semi-finished products based on them for further use in special food product technologies.

Structuring agents are needed to develop emulsified sauce products based on whey proteins. Excellent structuring properties distinguish plant raw materials with a high content of pectin substances. Pumpkin pulp can be used as such raw material, characterized by potential properties of structuring agents, structure stabilizers, and regulators of sensory indicators of food products. However, in its untreated form, the amount of pectins is insufficient for use as structuring agents.

Based on previous research, a protein-carbohydrate semi-finished product based on low-lactose condensed whey and fermented pumpkin puree (SFLLW) was developed [10]. However, the issue of researching emulsified sauce products based on it was not fully explored.

Therefore, this monograph chapter is dedicated to investigating the quality of emulsified sauces, using mayonnaise as an example, with the utilization of semi-finished based on low lactose whey.

6.2 Organization and research methods

An **innovative strategy** for developing emulsified sauce technology has been proposed to address physiological, raw material, environmental, technological, and economic issues.

In this regard, the main principles of mayonnaise sauce development and requirements for its technological properties were formulated. It should:

1. Meet the needs for essential nutrients of individuals with malabsorption who have restrictions on lactose consumption and egg intolerance.

2. Be aggregate-stable immediately after production and during storage.

3. Be produced from locally available raw materials in Ukraine with the realization of their food and functional-technological properties.

4. Reduce the volumes of secondary raw dairy materials (unused milk whey), which are potential environmental pollutants.

5. Make the technological process of sauce production based on SFLLW accessible to both high-capacity productions, small craft manufactories and restaurant establishments.

Implementing these principles is possible only through reasoned and targeted influence on the selected dairy and plant raw materials to most fully utilize their technological properties.

Based on the provisions of the innovative development strategy, a working hypothesis was formulated, which suggests that the use of plant raw materials as a source of low-esterified pectin substances and fermented milk whey as a source of proteins, calcium, phosphorus, low-lactose, with directed regulation of functional-technological properties during fermentation and thickening, using a low-lactose semi-finished product based on whey, will allow obtaining functional emulsified sauce.

The **aim** of the work is to investigate the rheological properties of model sauce systems, based on SFLLW, condensed fermented whey with reduced lactose content, and fermented pumpkin puree with increased pectin content.

The **object** of the research is the technology of mayonnaise emulsion sauce based on SFLLW and its quality.

The **subject** of the research is SFLLW, functional-technological properties of model systems based on SFLLW, and the quality of the developed culinary products.

The properties of "Provansal with 67 % fat content" mayonnaise of the classic recipe were investigated as a control sample by own production.

The basis for SFLLW used in sauce production owes its excellent emulsifying properties to its composition.

Model compositions of SFLLW with FMPP content exceeding 60 % and CLLW content lower than 40 % exhibited unsatisfactory organoleptic characteristics; therefore, they were not used for further research.

To produce SFLLW, pre-fermented milk whey is condensed under vacuum. The condensing process occurs at a reduced pressure of $P = -0.1$ Pa, at a constant temperature of 50 ± 2 °C, for 6·3600 sec. The concentration factor is 10 [11]. As a result of condensation, the effective viscosity index increases, providing grounds for using condensed in vacuo low-lactose milk whey (CLLW) in viscoelastic systems. Adjusting the acidity of CLLW to neutral pH levels is achieved.

Simultaneously, preliminary hydrothermal treatment of pumpkin pulp was carried out, followed by fermentation with enzyme preparation Vetom 1.1. The optimal parameters for the fermentation process in the production of fermented mashed pumpkin pulp (FMPP), which leads to the maximum accumulation of soluble pectin, are a temperature of 55 ± 3 °C, a duration of 15·3600 sec, and a concentration of enzyme preparation of 1.5 % [12].

A key issue in determining the functional-technological properties of the semi-finished product and its nutritional and biological value is establishing a rational ratio of system components.

One of the main requirements for sauce production based on SFLLW is the presence of the necessary texture and the ability to maintain structural characteristics. During the production of emulsion sauces, viscosity (η, Pa·sec) and stability (V, %) are the most indicative parameters during the emulsification stage. These parameters are directly dependent on the pH values of the emulsion system, emulsification temperature (t, °C), oil dripping speed (ν, ml/sec), and the speed of rotation of the mixer's working element (V, 1/sec).

The SFLLW content in sauce model systems varied within 40…90 % with a step of 10 %. The mixture components were stirred at a temperature of 20 ± 1 °C for duration of 60 sec until homogeneity was achieved using the IKA Ultra-Turrax T18 basic homogenizer at $V = 11200$ RPM.

The oil droplet size of the emulsions was observed using a Biological digital microscope MICROmed XS-3330 LED, and the volume-weighted diameter (DS, nm) was recorded, where DSD shows the % number of particles with diameter d_i. The measurement was used to provide distribution patterns of the oil droplet sizes.

The effective viscosity was determined using the rotational viscometer BPN-0.2M. The working temperature in the thermostat was $+23.3 \pm 1.5$ °C. Up to five rotation period values were taken for a fixed voltage value, excluding gross errors, and the average value was calculated. The samples' shear stress limit (SSL) was determined by extrapolating the linear section of the curve $\tau = f(\gamma)$ at a shear

rate of 100 1/sec, corresponding to values during sensory evaluation during product consumption.

The fat-binding capacity was determined by the amount of vegetable oil (sunflower) required to reach the inversion point. Determination of the phase inversion point to assess the emulsifying ability of model systems was carried out according to the method of O. M. Gurov [13]. Oil was emulsified using the DLH mechanical top-drive mixer with a dissolving attachment, mixing material from top to bottom and bottom to top under high turbulence and cross-force action for 25–35 min, depending on the component ratio. Emulsion stability (ES) was determined by the amount of unlayered emulsion. The emulsion type was determined by dilution in water. The phase inversion point value corresponded to the mass content of oil used in the process.

6.3 Investigation of the rheological properties of model emulsion sauce systems

Various interactions may occur in systems containing milk whey proteins and esterified pectin derived from fermented pumpkin puree. Depending on the temperature, processing time, pH of the medium, ionic strength of the solution, and the ratio of proteins to pectin, complexes may form (intra-molecular, inter-molecular, electron-neutral, charged coacervates) [9]. Therefore, it is advisable to investigate the nature of the interaction between pectin-containing FMPP and whey proteins in CLLW. To assess the effectiveness of SFLLW application, model compositions were studied at different ratios of FMPP to CLLW and amounts of emulsified oil.

The new mayonnaise composition was prepared using CLLW in combination with FMPP at different ratios as an emulsifier. Sample of mayonnaise by own production stabilized with egg yolk powder, was used as control for comparison. The dispersion characteristics were observed visually using a microscope, and the number of oil droplets of different sizes was counted. The results of the calculated average values of the size of emulsified oil droplets in different samples, taking into account the error, are shown in **Fig. 6.1**.

Lower stability was clearly observed for the control sample and the sample with a 90:10 ratio, as indicated by its higher average droplet size. Compared to these samples, those with ratios of 70:30, 60:40, and 50:50 had smaller average oil droplet sizes. This correlated with optical images of the emulsions. The results demonstrated the feasibility of using SFLLW as an emulsifier for preparing emulsion sauce, as expected from its strong emulsifying ability, as previously demonstrated [14].

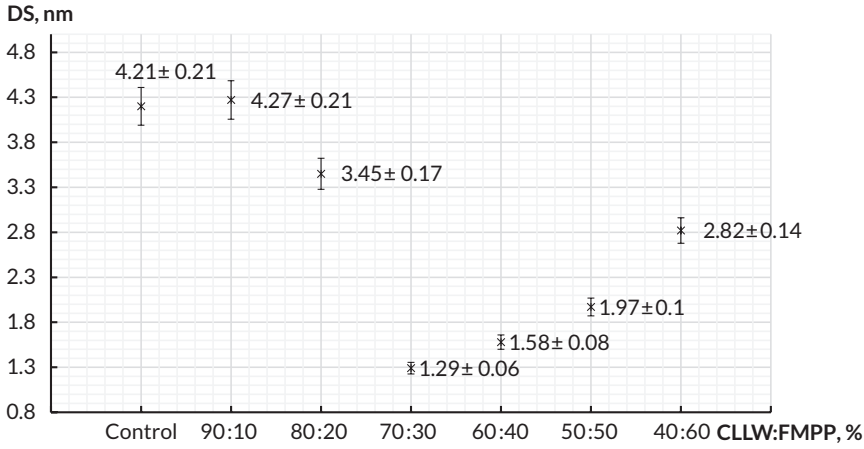

Fig. 6.1 Differences in oil droplet sizes (DS, nm) of emulsion depending on the nature composition of model systems

However, using FMPP in quantities of 30 % and 40 % of the SFLLW mass resulted in smaller droplet sizes. Consequently, this explains the increased physical stability of freshly prepared mayonnaises in these model compositions. The addition of FMPP in quantities of 30 % and 40 % of the SFLLW mass is attributed to improved interfacial activity of whey proteins due to changes in hydrophilicity and hydrophobicity balance, as well as molecular flexibility in the presence of pectins.

For the control sample, a wide range of emulsion droplet sizes was observed (**Fig. 6.2**), with the majority being large in size, indicating lower stability of the control sample.

In comparison to the control, samples with CLLW in the main component ratio of CLLW:FMPP in amounts of 70:30 and 60:40 not only had smaller oil droplets but also showed a denser grouping of sizes. There are sharp peaks in the curves shown in **Fig. 6.2**, indicating high homogeneity of the emulsified droplets in terms of size. However, for the sample with a CLLW:FMPP ratio of 50:50, the droplet size distribution curve was fragmented, indicating the presence of more homogeneous droplets in size and a small but significant number of large droplets. This indicates the reduced stability of such a system, which is consistent with optical images of the investigated emulsion sauces.

The rest of the samples showed significant variations in the ratio of droplet sizes. Although the average sizes of the 40:60 and 80:20 CLLW:FMPP samples were smaller than the control, these systems had significantly lower stability as they tended to separate more rapidly due to uneven droplet distribution. The obtained

results demonstrated the effectiveness of using SFLLW as an emulsifier for preparing egg-free mayonnaise, as could be expected from its powerful emulsifying ability, as shown in **Fig. 6.1**, **6.2**. However, using CLLW:FMPP in ratios of 70:30 and 60:40 resulted in smaller droplet sizes with a narrower size distribution structure. This trend corresponded to greater stability in these mayonnaise samples compared to the control sample.

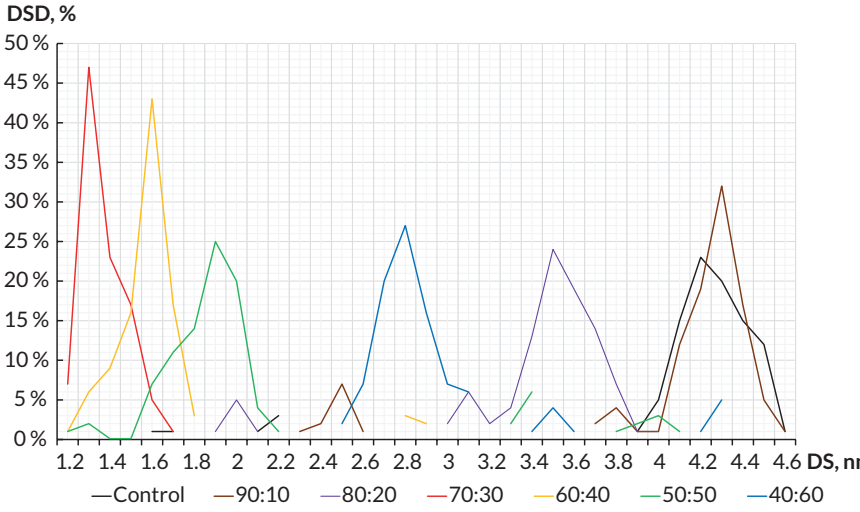

Fig. 6.2 Droplet size distribution patterns of sauce model systems

The interaction between whey proteins and pectin can be evaluated using rheological methods. Rheological methods of investigation can detect abnormal changes in viscosity and shear stress of systems, based on which it can be concluded whether substances interact or not. The results of effective viscosity studies of model systems are presented in **Fig. 6.3**.

As the FMPP content increased from 10 % to 60 %, the effective viscosity increased by 3.1 times. Therefore, it can be concluded that there is no coacervation of protein-pectin complexes and no thermodynamic incompatibility of proteins with pectins at the studied component ratios. In such cases, the viscosity of the system would decrease. The obtained data indicate the interaction of whey proteins and pectins with interpenetrating polymer network structures during micelle formation. This significantly affects the stability of the prepared emulsions. The obtained data were compared with the viscosity of the control sample prepared using a classic recipe.

A shear rate is constant and equal to 100 1/sec.

In a classic mayonnaise, the interaction between egg yolk proteins and oil droplets plays a crucial role in forming a network to stabilize the mayonnaise system. The higher emulsification rate of the control sample could be due to its lower viscosity and larger size of oil droplets in the emulsion (**Fig. 6.1, 6.2**), which reduces the emulsion's dispersing ability.

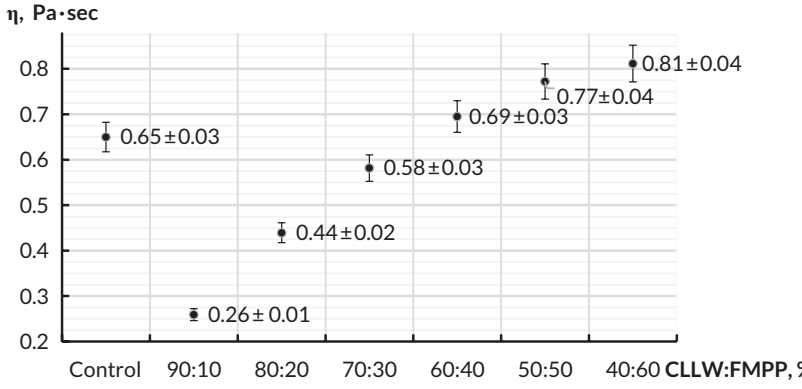

Fig. 6.3 Effective viscosity (η, Pa·sec) of model compositions on the CLLW: FMPP ratio

On the contrary, samples with CLLW:FMPP ratios of 40:60, 50:50, 60:40 exhibited higher viscosity compared to the control. The use of CLLW in combination with FMPP additionally improved the viscosity of mayonnaises, especially at higher FMPP concentrations. These results can be explained by inter- and intramolecular interactions between adsorbed proteins and pectins on the surface of oil droplets, leading to the formation of hydrocolloid networks. Simultaneous or sequential formation of interpenetrating polymeric mesh structures causes microphase separation of proteins and carbohydrates due to incompatibility arising from interchain nodes with subsequent oriented extrusion of pectin molecules onto the protein surface. Increased carbohydrate concentrations in microvolumes lead to enhanced self-association, hydrogen bonding, merging zones of pyranose pectin structures, resulting in faster viscosity growth. This process hampers pectin phase distribution, ensuring the necessary structuring of their structures and stabilizing the system's structure. Furthermore, water-soluble pectins with hydrophilic nature can effectively interact with water, increasing emulsion viscosity. Enhanced viscosity of the water phase can limit oil droplet movement, restricting collision between droplets, leading to improved emulsion stability. Additionally, visible viscosity is closely related to

mouthfeel, indicating a velvety texture of food emulsions. Thus, increased mayonnaise viscosity due to SFLLW usage can lead to improved textural characteristics of the product.

Determining the magnitude and dependence of the shear stress limit (SSL) on the component content allows for identifying the possible type of interaction and characterizing the rheological behavior of the systems. It has been established that with an increase in the FMPP content, the shear stress limit also increases. It should be noted that the dependence of SSL on the puree content shows the presence of a breaking point on the curve for the sample with CLLW:FMPP ratios of 70:30 (**Fig. 6.4**).

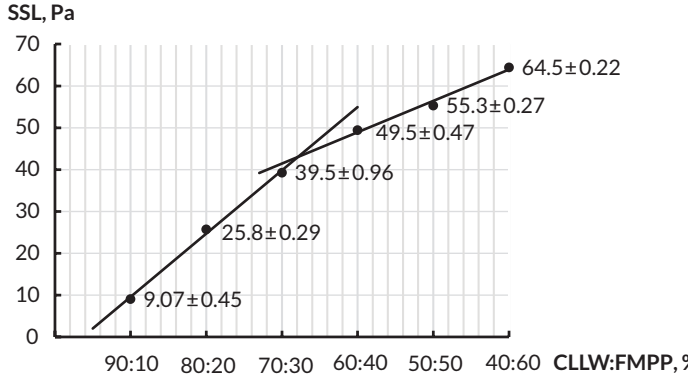

Fig. 6.4 Dependence of SSL (Pa) of systems on the CLLW:FMPP ratio

The break in the curve in **Fig. 6.4** indicates a change in the interaction between proteins and pectins. An increase in the structure-forming ability was observed for the sample with CLLW:FMPP ratios of 70:30. Based on the obtained data, it can be stated that at this ratio of components, SFLLW achieves maximum realization of structure-forming properties during emulsification, and the systems are characterized as visco-plastic. Further, an increase in SSL results from changes in the interaction between whey proteins and pectin. This is evidenced by the SSL rate increase. Presumably, the solubility of complexes, molecular weight, and diffusion coefficient change, which is consistent with studies showing that with an increase in pectin content, the size of protein-pectin particles also increases.

The investigation of shear rate is useful for sensory evaluation of consistency and overall appearance of samples. Since the addition of SFLLW increases the viscosity of mayonnaise due to its high ability to bind free water and oil as stabilizers for the continuous phase. However, samples with CLLW:FMPP at a ratio of 40:60 quickly

transitioned from a stage of maximum viscosity to emulsion stratification, indicating insufficient strength of complexes with lower protein content.

It can be concluded that by incorporating SFLLW into the composition of model emulsion sauce systems, it is possible to regulate viscosity over a wide range as a stability factor. Since the effective viscosity opposes the oil emulsification process, leading to significant energy consumption, it is necessary to evaluate the emulsifying capacity of the system. The emulsifying capacity of model systems was assessed by the phase inversion point (**Fig. 6.5**), i.e., conditions under which the system stratifies were determined.

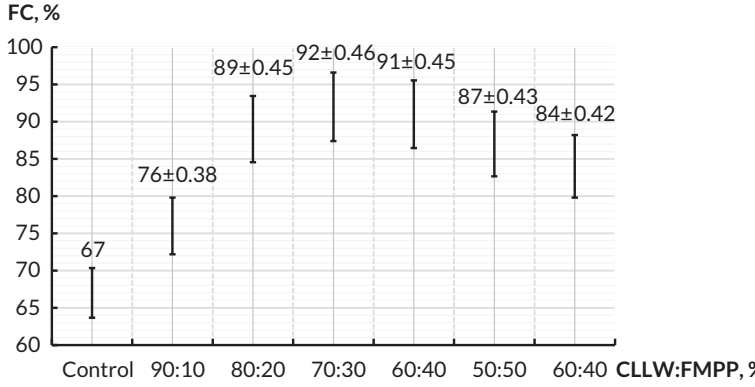

Fig. 6.5 Dependence of the emulsion inversion point (FC, %) of systems on the CLLW:FMPP ratio

To study the behavior of the system and determine the standard inversion point, an analysis of the recipe composition using SFLLW for different ratios of CLLW and FMPP, corresponding to different viscosities, was performed.

To determine the standard inversion point, each pre-balanced sample continued to be emulsified under unchanged system parameters: the stirring speed of the agitator, ambient temperature, and oil dripping rate. The variable was the amount of emulsified oil at which the system stratified.

It has been established that the dependence of the inversion point on the component ratio has an extreme character. In the interval of FMPP content of 0…30 % in SFLLW, the emulsifying capacity increases. A further increase to 40…60 % leads, on the contrary, to a decrease in the emulsifying capacity of the systems by 1.3 times. In systems using CLLW:FMPP at a ratio of 70:30, the phase inversion point of the emulsion corresponds to a fat content of 91…92 %. This is probably due to the

formation of complex protein-carbohydrate complexes, the maximum hydrophobicity of which is formed in systems with an FMPP content of 30 %.

With an FMPP content of more than 40 %, the hydrophilic-lipophilic balance may change, dimensional characteristics increase, and as a result, the diffusion coefficient decreases. This negatively affects the emulsifying capacity.

The conducted studies of emulsion stability during emulsification indicate that with an increase in oil content, the stability of the emulsion increases. However, an important factor is the influence of the oil dripping rate, which directly affects the stability of emulsions and the amount of emulsified oil. The optimal emulsification rate of the oil was determined under conditions of constant stirring speeds of the agitator and ambient temperature. The range of analyzed oil dripping rates was 0.09…0.11 ml/s.

As can be seen from **Fig. 6.6**, the effective viscosity index is directly proportional to the oil dripping intensity during its emulsification process. The rational viscosity zone corresponds to effective viscosity indices in the range from 0.586 Pa·sec to 0.640 Pa·sec. These viscosity values corresponded to an oil dripping rate of 0.05 and 0.1 ml/sec. Increasing the oil flow intensity to 0.2…0.4 ml/sec resulted in incomplete emulsification and accelerated the time to emulsion inversion. At the same time, reducing the flow intensity to 0.01 ml/sec led to stratification of the system already at 70 % of the added oil, which is explained by the non-uniform distribution of the oil phase under the established stirring regimes.

Therefore, a model system with CLLW:FMPP in a ratio of 70:30 and oil content of 60 %, with emulsion stability of 98 ± 2 %, is achieved, which meets the requirements of mayonnaise products according to regulatory documentation.

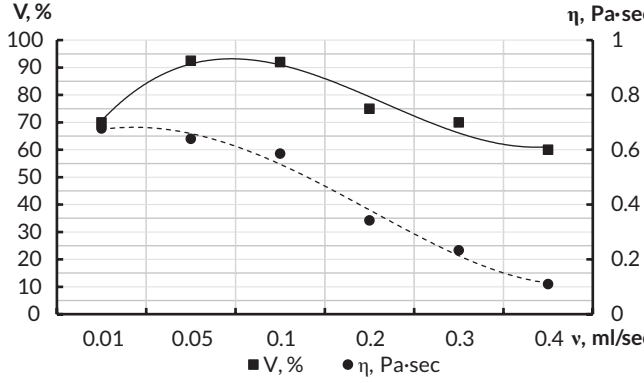

Fig. 6.6 Dependence of the emulsion inversion point (FC, %) and effective viscosity (η, Pa·sec) depends on the oil dripping rate (ν, ml/sec)

It is worth noting that in systems with an oil content of up to 60 % and FMPP content of 40…60 % in SFLLW, emulsion stability remains practically unchanged. However, the system's viscosity based on SFLLW increases in this range. Therefore, it can be assumed that different complexes are formed based on their surface activity and hydrodynamic properties (size, charge, molecular weight) at FMPP contents up to 30 % and at FMPP contents of 40…60 %.

Based on the analysis of the absolute values of emulsifying capacity and emulsion stability, it is possible to recommend a rational ratio of components in model systems based on SFLLW for obtaining emulsion-type sauces, like mayonnaise without egg-products.

Thus, the provided data indicate that using SFLLW to acquire certain functional-technological properties has several advantages. Firstly, this includes increasing the nutritional and biological value and providing products with therapeutic and prophylactic characteristics. Secondly, FMPP is capable of retaining moisture in the product structure, increasing stability, and enhancing the viscosity of emulsion-type sauces with high oil content. Thirdly, in this case, FMPP acts as a colorant and CLLW as a flavor enhancer.

Conclusions

The proposed innovative model for producing emulsion sauces similar to mayonnaise of the new generation involves the use of SFLLW as the main component, which acts as an emulsifier due to the presence of whey proteins and as a structure former due to its high content of soluble pectin.

As a result of the conducted research, the range of values of rational parameters for individual indicators of the technological process of preparing such emulsion sauces has been determined. Therefore, it is objectively justified to establish optimal values.

Studies of rheological and functional-technological properties have allowed to establish that with an increase in the FMPP content, the shear stress of model systems increases. Based on the obtained data, it is stated that with an FMPP content of 30 %, the maximum realization of structure-forming properties is achieved, and the systems are characterized as visco-plastic.

Based on the results of the research on rheological and functional-technological properties, a rational ratio of CLLW:FMPP as 70:30 and 60:40 is substantiated. Such a ratio exhibits high emulsifying and stabilizing properties, allowing to obtain emulsion systems with maximum stability at an oil content of 60 %.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 7

Crafting fermented pepper-based hot sauces

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Kateryna Sefikhanova

Abstract

In today's business environment in the food industry, business entities need to focus on improving and diversifying the range of products and dishes offered on the consumer food market. This requires the development and implementation of innovative technologies in production, focusing not only on the nutritional value of products, but also on their usefulness and compliance with individual consumer needs.

Currently, the creation of a variety of new products to improve the nutritional status of humans is a timely and relevant issue facing food scientists. Food technologies use functional ingredients with enhanced protective and improved technological properties.

The article analyzes the essence of the technology of craft hot sauces, systematizes the theoretical basis and methodological developments on the information base on the technology of production of craft hot sauces for restaurant business enterprises in modern economic conditions. A corresponding analysis of the principles, features and practical experience of craft production of hot sauces is carried out. A comparative analysis of the technology for the production of craft hot sauces by characteristic properties is carried out. Based on the results of the scientific research, the advantages of using innovative technologies for the production of hot sauces in craft production are determined. The importance of taking into account changes in tastes and consumer priorities in the nutrition of visitors to restaurant establishments is emphasized.

Comprehensive studies allow to state with confidence that the use of available vegetable raw materials and raw materials with high nutritional value allows expanding the range of craft sauces for restaurant business enterprises.

It is proved that when creating new compositions of hot sauces to ensure the guarantee of their production with the necessary structural, mechanical and organoleptic properties, the choice and justification of the use of natural resource raw materials for the recipe ingredients, their rational combination are taken into account.

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Keywords
Craft production, restaurant, hot pepper, fermentation, biological value, functional properties, organoleptic indicators.

7.1 Introduction

In the food industry, business entities face the issue of improving and diversifying the products and dishes offered on the consumer market, which requires the need to develop and implement innovative technologies, focus not only on their nutritional value, but also on their usefulness and individualization of demand. In the modern world, where the pace of life is rapidly increasing, and the daily rhythm becomes more stressful, sauces have become an integral part of culinary culture. Considering the globalization of culinary preferences, exotic flavors and non-traditional seasonings are increasingly found in sauces. These products have numerous advantages and simplify the cooking process, making it more efficient and convenient. Sauces allow for a wide range of flavors and aromas in culinary use. With their diverse palette of tastes, they can be successfully used to prepare various dishes, from classic to exotic. Most importantly, sauces can be a beneficial addition to a balanced diet and have functional properties. The richness of vitamins, minerals, and antioxidants in some of them makes these products not only tasty but also beneficial for health. Including plant-based ingredients in their composition can help combat hidden hunger, providing the body with necessary phytonutrients [1]. Additionally, sauces have high added value, and their production is quite profitable. The results of market research have confirmed the need for the creation of new types of food products made using only natural ingredients as stabilizers and flavorings [2]. The combination of high-quality raw materials will make it possible to produce a product with a balanced composition of nutrients.

This, for the most part, necessitates planning production processes with due regard to a set of optimization measures – economic, financial, organizational, technological, environmental, etc. In a competitive environment, a vivid example of adaptation to the conditions of uncertainty, risk and crisis is the activity of restaurants. For effective operation, they must find their unique product proposition in the consumer market, which involves not only organizing customer service processes, service, but also expanding the range at optimal costs without sacrificing quality.

An example is the use of a palette of sauces for various dishes. Sauce is an additional component with a liquid or semi-liquid consistency that is used in the cooking process or served with the finished dish to improve the taste and flavor. In modern cuisine, they are an integral part of a wide range of hot and cold dishes, appetizers, desserts, etc. [3].

Sauces can be classified according to various criteria, including geographic origin (for example, Italian, Indian, Japanese sauces, etc.), serving temperature (for example, hot or cold sauces), flavor (for example, mild or spicy sauces), acidity (for example, low-acidity sauces or acidic ones), sweetness (for example, sweet or savory sauces), color (for example, brown sauces, pink sauces, green sauces, etc.) [4]. Different condiments with varying sensory profiles are preferred and regularly consumed by people of different ethnic groups in different countries. Soy sauce is the leading condiment in Asian markets, with up to 5,876,000, 856,000, and 420,000 metric tons used annually in China, Japan, and Indonesia, respectively. This compares to some 679,600 metric tons of ketchup that was consumed in the United States in 2013, and approximately 333,000, 285,000, and 37,000 metric tons of fish sauce consumed in Vietnam, Thailand, and Myanmar, respectively [5]. Over the past 5–10 years, sauces made using the so-called "craft" method have become particularly popular, due to the growth of private family-owned small businesses and farms, where, in particular, it is possible to carry out a full range of production processes – "from field to table". Craft production differs from mass industrial production, first of all, in that production is carried out without the use of its characteristic technologies and at low capacity, i.e. it refers to small enterprises. Craft producers can manufacture products in small batches and cater to both traditional and exotic consumer tastes. Hot and spicy sauces are an integral part of the traditional cuisine in Asian, South American, and American countries. For most European consumers, hot sauces are considered exotic and are consumed in small quantities.

The number of consumers who focus on and show increased interest in the chemical composition, nutritional value, and presence of functional ingredients in food products is rapidly growing. This is driven by the issue of unbalanced nutrition due to the consumption of refined, processed foods, at a time when a healthy diet requires saturation with dietary fibers, vitamins, micronutrients, minerals, unsaturated fatty acids, etc. Taking into account the growing interest in healthy eating, the consumer food market is in need of products with increased nutritional value, enriched with biologically active components and excellent organoleptic characteristics. This effect can be achieved through the use of non-traditional plant raw materials in the production technology.

The production of food products with improved chemical composition and increased content of bioactive substances is one of the most pressing issues. This problem can be solved through the development and use of food technologies that combine different types of raw materials, which will ensure high quality of the finished product.

As practice shows, the sauces that meet the criteria of enhanced nutritional value positioned as "healthy food" or possess functional properties are the most popular. Therefore, expanding the range of craft sauces with increased nutritional value for HORECA sector enterprises is a relevant task.

7.2 Requirements for the production of craft sauces

The concept of "craft sauce" is associated with such definitions as uniqueness of recipe, use of natural ingredients, and application of technologies that allow for maximum preservation of freshness and flavor of quality components of the product.

If to analyze the norms and requirements for the design and recipe of craft products and dishes, it is worth noting the absence of strict requirements for their production technology. The main principle, as mentioned above, should be, as a result of predominantly manual and family labor at all stages of the production process, a guarantee of the absence of artificial preservatives, colorants, food additives and chemical ingredients. However, this is not a reason for craft producers to ignore the need to obtain relevant certificates and meet sanitary requirements. Thus, in order to sell craft products, entrepreneurs must have all the certificates of health safety required by the current legislation of the country where the craft food is produced. In fact, each craft product has a unique recipe, which determines the high quality of such a unique product. It is worth noting that the technology of manufacturing craft products involves careful quality control of the selection of all components without exception and their combination based on a unique recipe. In this case, the manufacturer's skill is of great importance. Practice proves the uniqueness of a craft product throughout the entire cycle – from growing or purchasing the right kind of natural ingredients (raw materials) from producers to selling it to the consumer in its original packaging, where attention should be focused on the uniqueness and natural ingredients and the environmental orientation of the technology of both product production and packaging.

In fact, there is currently no legislatively defined concept of "craft production" in Ukraine, which, given the national nature of production, requires compliance with certain criteria, including the predominance of manual labor rather than mechanized labor; only high-quality raw materials are used. The philosophy of a craft product is based on responsibility to the consumer, the desire to match the general culture of consumption with the indicator of quality and significance. At present, there are no legislatively defined requirements for the area, volume, and capacity of craft production in Ukraine, i.e. it can be either small or large-scale production. The only exceptions are restrictions on those industries that require a certain type of license permit, which is granted separately for the manufacture of the product and for the sale, for example, beer from a craft brewery. With regard to the differences between mass production and craft production, it is advisable to take into account the experimental nature of such production, driven by the desire

to achieve the highest, sometimes original taste, which affects pricing and requires intensifying the search for its own consumers and taking into account changing tastes. For such activities as "artisanal", which relate to the smallest producers and family food producers, favorable conditions are created to attract donors, financial support for the development of family businesses and the development of rural communities.

However, sanitary regulations apply to enterprises involved in food production, regardless of ownership form and departmental subordination, and must be fully complied with. A threat to food safety may be posed by a biological, chemical or physical agent in food that may cause adverse health effects. Food safety is ensured by the joint efforts of all participants in the food chain.

Culinary products are produced in the form of dishes, culinary products and culinary semi-finished products that differ in their main characteristics (**Fig. 7.1**).

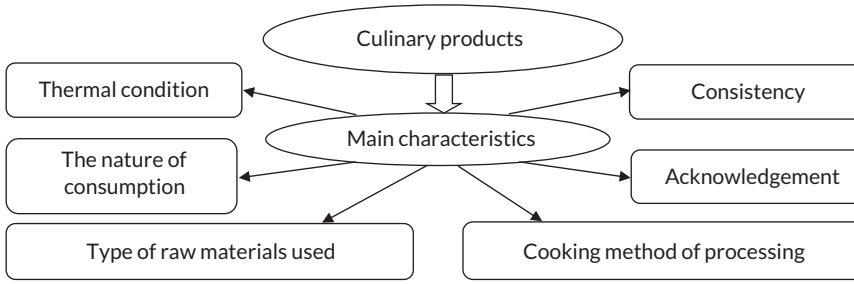

Fig. 7.1 Main characteristics of culinary products

Hygienic standards for microbiological indicators include control over four groups of microorganisms: sanitary indicators, potentially pathogenic microorganisms, pathogenic microorganisms, and microorganisms that cause product spoilage [6]. Microbiological standards also apply to products of intensive technologies: using microwave and infrared heating, as well as to products made from fermented raw materials, which is of interest and important when applying the technology of hot sauce production. Regarding compliance with microbiological standards for sauces or dressings for second courses produced by catering companies for garnishes, here are examples. In particular, the total number of mesophilic aerobic and facultative anaerobic microorganisms CFU should not exceed 3.5·10 in 1 g/cm^3; the mass of the product in which BCCP (coliforms) is not allowed is 1.0 g/cm^3; the mass of the product in which *E.coli* is not allowed is 0.1 g/cm^3; the mass of the product in which *S.aureus* is not allowed is 5 g/cm^3 [6].

7.3 Assortment and ingredients of hot sauces

There are many variations and names of hot sauces. In fact, every culture has its own original sauces, including spicy ones, as natural ingredients for them are mostly grown within the territory of a particular country and are characteristic of that country, corresponding to its culinary traditions. Even within one country, seemingly similar sauces differ in ingredients, their proportions, and technological features. Currently, in Ukraine, hot sauces from craft producers have their own differences not only due to natural raw materials, but also due to the manufacturing technology. The advantage of hot sauces is their inherent ability not only to enrich the taste of dishes, but also to create new dishes based on hot sauce, thereby creating conditions for expanding menu offerings.

In such European countries as those located in the north and east, hot sauces are popular as a seasoning for almost all types of meat, fish, poultry, vegetables and are popular in Germany, Alsace, many countries of Central and Eastern Europe, etc. In England, for example, hot sauces are used to enrich the flavors of roast beef and in the United States, fast food restaurants use hot sauces.

Ukrainians, according to their culinary preferences, tend to lean towards European cuisine. Therefore, hot and spicy sauces are used here significantly less than in Asian or American cuisine. Traditionally, spicy sauces made from the seeds of plants such as white mustard (*Sinapis alba*), brown mustard (*Brassica juncea*), black mustard (*Brassica nigra*), and horseradish root (*Armoracia rusticana*) are widely popular.

Mustard seed is good source of protein, fiber, minerals, vitamins, antioxidants, and phytonutrients. In addition, mustard is a source of valuable phytonutrients. Its main biologically active components are glucosinolates (sinigrin and sinalbin) and their breakdown products, rich in sulfur-containing isothiocyanates, phenolic compounds, and phytosterols. These compounds possess antioxidant, anti-inflammatory, anticancer, antimicrobial properties [7].

Mustard is a condiment sauce made from ground, often de-fatted mustard seeds, mixed into a paste with water, vinegar, salt, oil, and other spices, and then refined. By using different varieties of seeds and adjusting the concentrations of the main ingredient, milder or spicier sauces are obtained.

Horseradish or Armoracia rusticana is a perennial herbaceous plant in the Brassicaceae family, which also includes mustard, wasabi (sometimes called Japanese horseradish), cabbage, and broccoli. Horseradish is a popular culinary addition due to its ability to enhance the flavors of dishes and sauces, as well as its functional properties. In recent years, scientists have been paying increasing attention to horseradish due to its high content of biologically active compounds. The specificity of these

compounds gives horseradish antioxidant, antibacterial, fungicidal, and anti-tumor properties [8]. Like in mustard, the sharp, pungent taste of horseradish is attributed to glucosinolates. In addition to glucosinolates, horseradish contains many other antioxidants, some of which not only destroy and block free radicals, but also prevent the appearance of mutations that can occur in humans under the influence of adverse environmental conditions and side effects from taking medications, which in turn can increase the likelihood of developing various degenerative diseases [8]. In Ukraine, a moderately spicy snack called "Buriachky" of grated boiled beetroot, mixed with chopped fresh horseradish root, vinegar, sugar and salt, is traditionally cooked. A popular addition to meat dishes in Eastern Ukraine is grated horseradish mixed with thick cream. A traditional "Horseradish and Beetroot" spicy seasoning is produced on an industrial scale, where crashed horseradish roots are mixed with raw beetroot.

Many hot sauces are based on peppers (*Capsicum spp.*). The most common is considered to be chili sauce. Chili sauce is a condiment prepared from the edible portion of healthy and clean fresh chili peppers or processed chili, such as chili that has been roasted into powder, chopped, or pickled in vinegar or other acid. It may also contain mango, papaya, tamarind, tomatoes, garlic, onions, carrots, sweet potatoes, other spices and herbs, honey, and other edible ingredients [9].

Peppers are commonly considered vegetables, but from a botanical perspective, they are berries. Pepper varieties are classified based on the characteristics of their fruits, such as spiciness, color, fruit shape, as well as their usage. When ripe pods of red peppers are dried and ground, they become the most consumed spice in the world. Practically all pepper varieties cultivated for commercial purposes in the USA belong to the species Capsicum annum. However, one main type, "Tabasco", belongs to Capsicum frutescens. Two other pepper species gaining popularity are Capsicum chinense, "Habanero" and "Rocotillo", and Capsicum pubescens, "Peron" and "Manzano" [10].

Hot pepper is the only plant crop that contains capsaicin. Recent scientific studies have shown that capsaicin contained in hot peppers has antimutagenic and antitumor effects [11]. This component inhibits the growth of cancer cells, which confirms its effectiveness. The presence of this substance determines the beneficial properties of the product. According to research, the alkaloid capsaicin has a pronounced anti-inflammatory, analgesic and antioxidant effect. In addition, hot peppers help prevent oxidative stress, protecting cells from damage and keeping them young. Pepper contains vitamins B_1, B_2, A, E, C, P, as well as various trace elements that are essential for the normal functioning of the body, such as calcium, iron, phosphorus and silicon.

Hot pepper has beneficial properties because it acts as a natural preservative. Its complex components have antimicrobial and antibacterial effects that prevent the development of harmful microorganisms in foods.

As an example of research aimed at determining the antioxidant properties of certain plant species, it is advisable to consider the results of the study of Iranian chili pepper extract, for which some solvents, such as water, ethanol, and a water-ethanol solution, were used [12]. Two types of tools were used to influence the object of study, including with and without treatment with ultrasonic waves. The amount of tocopherol and phenolic compounds in the extracts was measured by the stoichiometric method, and the antioxidant capacity of the extracts was measured and analyzed using beta-carotene and DPPH tests. As a result, the oxidative stability of the extracts was determined. The data were statistically analyzed using analysis of variance (ANOVA) and Duncan's test. The level of $P<0.05$ was considered statistically significant. The maximum and minimum extraction efficiencies of phenol and tocopherol compounds were obtained using ethanol and water, respectively. Thus, due to its high antioxidant capacity, hot peppers can be widely used in the food industry.

The technology for preparing a special premium group of hot sauces involves the use of a pepper fermentation process. Sauces have a consistency from liquid to pasty, and can be moderately or extra hot. Also, hot sauces can differ in color – green, red, brown.

Among the variety of hot sauce formulations, in Ukraine, hot sauces based on peppers, such as "Chili", "Habanero", and "Trinidad Scorpion", are widely popular among consumers' taste preferences.

When we use the term "hot" sauce, we associatively understand that it refers to a certain degree of hotness. Nowadays, this hotness is given to hot sauces by the spicy ingredient capsaicin, which, when added to liquid and paste-like mixtures, contributes to the creation of the original flavor. Thanks to this spice, any dish can deepen its flavor.

Today, one of the most well-known hot sauce companies is Tabasco, which was actually the first to start packaging hot sauce in bottles. Among the well-known suppliers of hot sauces for HORECA are, in particular, those that offer exotic or author's hot sauces based on Scorpion Trinidad with BBQ and Habanero. Technologists and culinary specialists also offer new author's hot sauces, including, for example, the hot sauce Zapal Horeca, which is in demand among restaurateurs. There is also a constant demand for modernization of classic recipes in the restaurant industry. Especially popular in the world are recipes based on fruits, including pineapple, mango with the addition of habanero or chili peppers. However, it is worth noting a certain difference in the flavor properties of hot sauces depending on the region of their origin.

For a more detailed consideration of the features of hot sauce production technology, it is worth paying attention to the essence of the system that measures the

level of capsaicinoids in a particular substance. We are talking about spicy chemicals, not just capsaicin in a substance. This system is called the Scoville Scale in honor of the pharmacist Wilber Scoville, who developed this indicator in 1912, measured in Scoville Heat Units (SHU) and used to assess the spiciness of a particular dish. If this indicator is determined in a hot sauce, this system allows to find out the level of its burning sensation. Thus, if during a standard tasting there is a certain subjectivity in determining the hotness of a hot sauce, then by measuring chemicals on the Scoville scale, it is possible to obtain an objective result.

7.4 Features of the technology and organoleptic characteristics of hot craft sauces

Even during the COVID-19 quarantine and amid the war in Ukraine, the niche of craft food products and dishes based on natural ingredients and using environmentally friendly technologies continued to be enriched with new offers. Among other things, the range of craft hot pepper sauces is constantly expanding.

Pepper is one of the most profitable products for processing, as with the right approach, only the stem remains from the waste. The pepper itself goes into the sauce, and from the pomace, oil or spices can be made. The original processing and production technology of hot sauces was developed using fermentation methods, similar to how it was done in ancient times to preserve products, or made based on fermented peppers, i.e., those fermented in oak barrels.

The technology of making hot sauces requires taking into account all stages from preparation to growing plants to final production and packaging. Issues such as the method of growing peppers in heated greenhouses or two- to three-year storage of plants, measures to avoid over-pollination, fruit change processes, pungency and taste for the following years are addressed. Experiments are being conducted with different varieties, their yields and growing technology. In order to avoid cross-pollination, no more than 12–17 varieties of pepper are selected from at least 40–50 varieties of pepper for further use in the production of hot sauces based on the results of greenhouse experiments. In addition to the requirements for agro-technological issues, the technology for processing the pepper harvest and making sauces is also unique. The company uses its own development, cold fermentation, which makes it possible to produce the final product without preservatives. In fact, the company has developed a technology that "allowed it to avoid large-scale capital expenditures" and has proven to be effective. To produce a hot sauce of appropriate pungency and flavor, a number of requirements must be met. For example, peppers should not be watered

two weeks before harvesting, as this affects the pungency, which will increase due to the low amount of moisture. Pepper seeds are also a very important component.

The technology of making hot sauces by cold fermentation allows to produce the final product without preservatives and is unique, although its development requires too much time to determine the optimal mode. Fermentation during the experiments was carried out in both large and small metal containers. The search was made to ensure sufficiently moistened wort and to protect it from oxygen. An important aspect of developing the technology for the production of craft hot sauces was that it was necessary to develop a technology that would avoid large-scale capital expenditures and be effective at the same time.

For the production of hot sauces, the fermentation method is used, similar to the process of creating red wine, which allows to avoid oxidation of flavoring substances and preserve their bouquet in the finished product. The peculiarity of fermentation is that this process can also occur without the participation of microorganisms. In this case, fermentation occurs exclusively due to the tissue's own enzymes, which are subject to such treatment, and the fermentation process takes place on the cut, i.e., in the presence of air oxygen, polyphenol oxidases oxidize polyphenols and quinones are formed. In turn, quinones oxidize amino acids and as a result, melanin, a brown pigment, is formed.

It is important to distinguish the fermentation process from the process of industrial cultivation of microorganisms in bioreactors to produce a variety of valuable products, from biofuels to animal protein substitutes and antibodies. There is also a difference between the fermentation process and the technology of using enzymes isolated from microorganisms to break down complex molecules, i.e., the method of enzymatic hydrolysis.

And although craft producers today emphasize the innovation of the fermentation technology for the production of hot sauces, it is fair to say that this method was actually used in one form or another by our distant ancestors. Today, fermented foods are back in the spotlight, mainly because of the positive health effects of fermented foods. In practice, fermentation is a unique biotechnological process that not only helps to preserve food and beverages for a long time, but also helps to significantly increase the nutritional value of products and create fundamentally new ones. As for the classification of fermented products, they are distinguished according to the type of raw materials and the methods of biochemical transformation of substances. Experiments have proven that different microorganisms are involved in the formation of all fermented products, where each species has its own role and result of its activity. It is worth noting that the majority of fruits, vegetables, cereals, and dairy products are fermented by the first type of fermentation, i.e. when lactic

acid fermentation accumulates organic acids, which lead to a decrease in pH and the appearance of an acidic taste, as well as change the texture of the product and can increase its nutritional value. It is important to realize that in this case, the human body absorbs these fermentation products better due to the increased solubility of mineral elements [13].

Most traditional fermented foods are characterized by a complex combination of the vital processes of various microorganisms. Almost all vegetables and their mixtures contain sugars, which are used in the fermentation process. Among the most popular vegetables for fermentation are cabbage, cucumbers, and olives. In fact, all parts of the plant are a natural environment for a wide variety of microorganisms, including bacteria, yeast, and molds. Due to the contact of plant surfaces with atmospheric air, it is almost impossible to avoid the appearance of aerobic bacteria, fungi and facultative anaerobes that can exist both in the presence of oxygen and in its absence. On plants, lactic acid bacteria, which are anaerobes and therefore die from oxygen, may be present in small quantities.

The process of lactic acid fermentation is characterized by the following features: after a number of bacteria that grow differently in the fermentation medium for a certain period of time have undergone the process of fermentation, their growth is inhibited or stopped due to the accumulation of metabolic products; then another group of bacteria develops in the anaerobic environment. If anaerobic conditions are not maintained, i.e., there is access to atmospheric air, aerobic bacteria and fungi begin to develop to replace lactic acid bacteria, which causes rotting and mold formation.

When making pepper sauce, the fruits are first processed into a homogeneous mass, then a few hours later, the process of lactic acid fermentation takes place, which can last from one to several weeks. While there is still some oxygen in the pepper wort tank, facultative anaerobes dominate among the bacteria, but after 1–2 days in the absence of oxygen, lactic acid bacteria begin to prevail, which promotes the fermentation of sugars to lactic acid to produce a small amount of acetic acid and ethyl alcohol. At this stage of the fermentation process, intense carbon dioxide is released. Additional fermentation substrate can be created by the synthesis of enzymes by some bacteria. The resulting enzymes break down cell wall polysaccharides, including hemicelluloses, starch, pectins, and cellulose. As a result of the fermentation processes, which are quite complex, a significant amount of byproducts is recorded, including alcohols and organic acids, which, in turn, enter into an esterification reaction to form esters, volatile compounds with a pleasant odor. These processes contribute to the formation of new flavors in the fermented sauce, which distinguishes it from the smell of fresh pepper.

Also, due to the release of compounds contained in fresh pepper fruits, a unique bouquet of smells and flavors is formed in the sauce wort, i.e., the taste and aroma properties of the product are improved. At the same time, these substances inhibit the growth of yeast. As a result of the accumulation of acid in the sauce wort, its pH drops to 4.5, and the fermentation rate slows down. This is because under such conditions, only acid-resistant bacteria survive, which causes the fermentation of the remaining sugars. The fermentation process is eventually completed when the pH level is fixed at about 3.4. As a result, the growth of the vast majority of microorganisms is inhibited, which contributes to the increase of the shelf life of such wort in the absence of air access [14]. Thus, fermented hot sauce is rightly considered a unique product, the taste and pungency of which is influenced not only by the pepper fruit, but also by strains of bacteria and microorganisms that affect the fermentation process [15].

At the same time, the issue of intensifying the development of new recipes and technologies for culinary products for healthy eating, including sauces, remains insufficiently addressed.

Currently, Ukrainian scientists have proposed a number of scientific approaches to develop new types of sauces with the addition of functional ingredients. Ukrainian scientists continue to work on developing recipes for sauces with soluble dietary fiber, which helps to bind and remove anthropogenic pollutants and products of metabolic disorders from the body. The main condition for obtaining a high-quality sauce product should be to obtain a stable and uniform consistency that would protect against delamination when serving the sauce to the consumer, i.e., its viscosity is ensured [16]. When it comes to the appearance of sauces, in the HORECA sector, it's important to consider its significant impact on both the physiological and psychological perception of consumers. The sauce should be homogeneous in appearance, without films and fatty substances on the surface [16].

In recent years, foreign scientists have also obtained a number of positive results in developing new technologies for the production of sauces, including the study of the introduction of okra in natural and lyophilized forms into tomato sauce as a thickener and emulsifier of mucus; the proposed technology of natural sauce made from processed cheese flavored with essential oils; the development of a technology for enriching white sauces with red bell pepper and the determination of the sensory characteristics and consumer acceptability of new white sauces [17].

A rational recipe composition was experimentally selected and the production technology and assortment of craft hot sauces were developed (**Fig. 7.2**). The sauces are either made by salting, as was done in ancient times to preserve food, or made on the basis of fermented peppers, i.e. fermented in oak casks, with the addition of quince, pear and honey.

Fig. 7.2 Spicy craft sauces

The main factors that determine the state of human health are food safety and quality. Therefore, any development of food technology should include the study of these indicators. Usually, organoleptic properties are the first among the quality indicators to be studied. Sensory analysis allows to establish the patterns of formation of organoleptic indicators, since these are the indicators by which potential consumers primarily evaluate the product.

Assessing the quality of food products using the human senses is the oldest and most common method. Modern laboratory methods of analysis are more complex and require more effort compared to organoleptic evaluation, but they allow characterizing certain quality attributes. Organoleptic methods are fast, objective and reliable for the overall assessment of product quality. Sensory control allows to quickly and purposefully influence all stages of food production.

The developed hot sauces were subjected to an organoleptic analysis, which is important for food manufacturers, as it allows them to quickly assess the quality of not only finished products but also products at different stages of production. Identification of defects and shortcomings of semi-finished products allows timely correction of technological violations and prevention of low-quality finished products (**Table 7.1**).

According to the analysis presented in **Table 7.1**, it can be concluded that the developed spicy craft sauces have high taste quality, which will positively affect the perception of the new product.

During the research, a quality assessment system for hot sauces based on fermented peppers was developed, taking into account the importance of each criterion (**Table 7.2**), which allowed to demonstrate high organoleptic quality indicators of the products.

Table 7.1 Organoleptic characteristics of concentrated craft hot sauces

Name of indicators	Sauces names	
	Habanero sauce	Habanero sauce (pear, honey)
Appearance	Homogeneous, evenly mashed puree-like mass that does not spread on a horizontal surface	Homogeneous, evenly mashed puree-like mass that does not spread on a horizontal surface
Consistency	Homogeneous, without foreign inclusions	Homogeneous, without foreign inclusions
Color	Light yellow	Light yellow
Odor	With a pronounced flavor of pepper and quince	With a pronounced flavor of pepper, pear and honey
Taste	Spicy-sour-sweet with a pronounced quince aftertaste	Spicy-sour-sweet, with a pronounced pear and honey aftertaste

Table 7.2 Results of organoleptic analysis of craft hot sauces

Name of indicators	Weighting factor	Characteristic weighting factor	Features	Evaluation, points	
				Habanero sauce	Habanero sauce (pear, honey)
1	2	3	4	5	6
Appearance	0.2	0.83	Homogeneity	4.80	4.80
		0.17	Absence of inclusions	4.70	4.80
	Total score by indicator			**0.95**	**0.96**
Consistency	0.25	0.4	Homogeneity	4.80	4.90
		0.3	Density	4.70	4.70
		0.3	Fluidity	4.90	4.90
	Total score by indicator			**1.19**	**1.20**
Color	0.15	0.3	Intensity	4.70	4.90
		0.2	Expression	4.90	5.00
		0.2	Homogeneity	5.00	5.00
		0.3	Naturalness	5.00	4.80
	Total score by indicator			**0.74**	**0.74**
Taste	0.25	0.1	Balance	5.00	4.90
		0.2	Expressiveness	5.00	4.80
		0.1	Speed of release	5.00	5.00
		0.3	Naturalness	4.90	5.00
		0.3	Purity	4.90	5.00
	Total score by indicator			**1.24**	**1.24**

Continuation of Table 7.2

1	2	3	4	5	6
Odor	0.15	0.3	Purity	5.00	5.00
		0.2	Expressiveness	4.90	5.00
		0.2	Stability	4.90	4.90
		0.3	Compliance with the type of raw materials used	5.00	4.90
		Total score by indicator		**0.74**	**0.74**
		Overall assessment		**4.86**	**4.88**

The results of the tasting evaluation show an unambiguously positive response to the developed food product. The profiles of organoleptic quality assessment of hot craft sauces are shown in **Fig. 7.3**, **7.4**.

During the organoleptic analysis, it is found that the obtained sauces have high quality indicators in terms of organoleptic characteristics. The system of scoring the quality of sauces, taking into account the importance coefficient, shows that the overall score for sauces is as follows: for Habanero craft hot sauce – 4.86, for Habanero craft hot sauce (pear, honey) – 4.88. The developed craft sauces have a traditional taste that is positively perceived by consumers, which will contribute to the success of the innovative product.

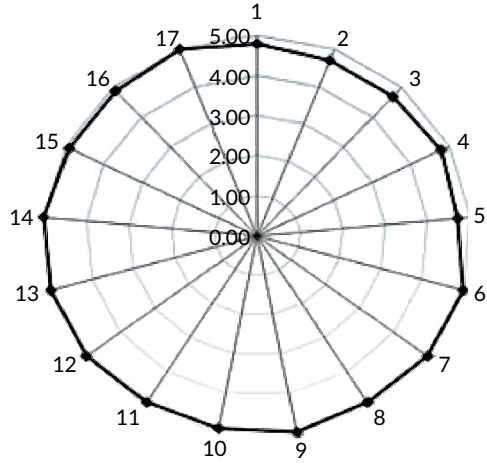

Fig. 7.3 Organoleptic profile of Habanero craft hot sauce

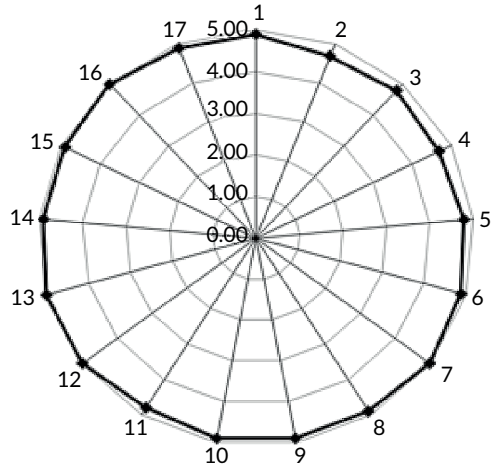

Fig. 7.4 Organoleptic profile of Habanero craft hot sauce (pear, honey)

Conclusions

Thus, even during times of war, the production of certain products in small batches with the processing of local raw materials by farmers and the manufacture of craft products based on it makes it possible to develop mini-enterprises in the food industry. These enterprises can operate during a state of war, require minimal capital investment, have a better understanding of the dynamics of the regional market, and take into account all aspects of the population's food needs.

In cooperation with research scientists and taking into account consumer demand, the fluctuations of which should be studied, it is possible to achieve positive results in the food industry and restaurant business. Among the various technologies for the production of hot sauces, including at craft enterprises, it is currently advisable to highlight the importance of fermentation technology as one that contributes to the creation of products with increased nutritional value and unique properties and health benefits. It is recommended to pay special attention to the cold fermentation technology, which is used in Ukraine to produce hot sauces directly at craft enterprises.

Given the wide range of topical areas of research, to reveal the essence of the stated topic, the results of monitoring the state and processes and technology of developing hot sauces at small businesses, in particular family-type enterprises

operating in Ukraine, are mainly presented. The author also analyzes the current regulatory framework in Ukraine on the production of sauces, the organization and features of craft food production, the principles of operation of restaurant business enterprises in the current business environment and their motivating factors for using hot sauces in their production activities. It is proved that when creating new compositions of hot sauces to ensure the guarantee of their production with the necessary organoleptic properties, it is important to take into account the choice and justification of natural resource raw materials for the recipe ingredients, their rational combination.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 8

Biological activity of phenolic compounds of oats depending on the technology of its use in feeding geese

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Abstract

Avenanthramide phenolic compounds are present in the composition of the green mass and seed oat grain. These compounds have powerful biological activity, however, the content of these compounds fluctuates significantly. The purpose of the conducted research was to determine the content of avenanthramides in the composition of the green mass of oats of the Spurt variety of milk-wax maturity and further optimization of the technology of using oats in feeding geese. The results of the chromatographic analysis of oat samples proved the presence of avenanthramides, tricin and oxylipins both in the grain and in the green mass of oats. A comparative study of the influence of the aqueous extract of the green mass of sowing oats and the green mass of oats in the geese diet on their development in ontogenesis and the biological value of the obtained meat was conducted. It has been established that under the influence of biologically active compounds of oats, the antioxidant activity of the muscle tissues of geese increased significantly during ontogenesis, which contributed to the increase in the nutritional value of the obtained meat. It has been proven that oat extract contributes to a more powerful activation of the antioxidant system of geese muscle tissues during the physiological stress of feather formation. However, a higher content of ω3- and ω6-polyunsaturated fatty acids of lipids in skeletal muscles after slaughter was established for geese that received green mass of oats. Addition of oat extract to the geese diet prolonged the state of pro-oxidant-antioxidant balance and contributed to an increase in the content of essential fatty acids in meat during 120 days of storage of whole goose carcasses.

The addition of oats and alfalfa to the geese diet led to an improvement in poultry meat yield and an increase in its protein content. A positive effect of oats and alfalfa

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on the ability of meat to retain moisture and loss of mass during defrosting was established. An increase in the content of ω3-polyunsaturated fatty acids, vitamin E, β-carotene and essential amino acids threonine and methionine was also observed. At the same time, the level content of other essential amino acids remained at the level of the meat of the control group.

In the thigh goose meat of the experimental group, during low-temperature storage, the processes of peroxide oxidation were activated 12 days later than in the corresponding samples of the control group. At the end of storage, the meat of the research group had a significantly higher content of vitamin E, β-carotene and ω3-PUFA. The content of essential amino acids valine, leucine and isoleucine in the experimental sample also exceeded the corresponding indicators of the control group.

Keywords

Sowing oats, avenanthramides, goose meat, end products of lipoperoxidation, vitamin E, β-carotene, fatty acids, amino acids.

Goose breeding is a traditional and promising sub-sector of poultry production in Ukraine. It does not compete with other agricultural industries, as goose farming can use land that is unsuitable for plowing and grazing. Goose breeding has a number of advantages over other poultry industries, namely: high quality meat, efficient use of feed, high growth rate, multifunctionality of goose products, natural pest control, frost resistance, etc. [1].

The COVID-19 pandemic has caused a sharp decline in poultry production and supply, resulting in serious economic losses on local and international markets. The war in Ukraine has significantly deteriorated the situation in our domestic agricultural market, including the poultry industry. The goose industry is particularly affected, as it is the one that primarily needs free pastures.

8.1 The use of biologically active substances of oats in feeding geese as a way to improve the quality of geese farming products

Among modern goose breeds, one of the most promising is the Legart Danish. These geese are characterized by early maturity and high feed conversion [2]. The meat of this breed of geese is considered dietary because fat accumulates in the subcutaneous layer. This feature makes it useful for a variety of diets and healthy eating. In addition, this breed of geese is characterized by low maintenance and rapid growth.

However, goose meat, due to its high content of unsaturated fatty acids, is highly susceptible to oxidative damage during storage. These processes adversely affect the quality of meat products, reduce the nutritional value of meat and shorten its shelf life [3–5]. One of the ways to counteract oxidative spoilage of poultry meat during storage is to use antioxidants, compounds that can inhibit the oxidation of fatty acids, primarily unsaturated ones. Providing the general population with quality food products requires the use of safe antioxidants of natural origin.

In recent years, consumers have been increasingly preferring more natural and less processed foods. The food industry is responding to this demand with clean-label products that use natural antioxidants and preservatives derived from plants. These ingredients not only extend the shelf life, but also bring health benefits. The positive impact of biologically active plant compounds on meat quality has been proven by many recent studies [6–9].

Since 1995, scientists of the TADTU under the leadership of Doctor of Agricultural Sciences, Professor V. Kalytko have been conducting research to determine the effect of synthetic and natural antioxidants on the development of poultry and the quality of meat. A reliable positive effect on the quality of poultry meat of grape seed extracts, dioecious nettle and other wild plants has been proven. In 2018, we started researching the effect of biologically active compounds of oats on the development of poultry and the quality of meat.

Oats (*Avena sativa L.*) is a cereal crop that is an important source of natural antioxidants and is noted for its numerous nutritional, medical, and pharmaceutical benefits. These antioxidants include flavonoids, phenols, saponins, tocopherols, and unique oat compounds called avenanthramides (AVNs) [10, 11]. The structure of avenanthramide molecules determines their multifunctionality, which provides protection against many diseases.

Scientists at the University of Wageningen proved [12] that the composition of seed oats contains 28 unique avenanthramides, including the new avenanthramide 6f. It has been found that the content of avenanthramides increases 25 times from seed to seedling. Avenanthramides 2p, 2c, and 2f, which are usually identified as the main avenanthramides, accounted for less than 20 % of their total content in seedlings. Therefore, quantitative analysis should include a wider range of avenanthramides to prevent underestimation of the total amount of these compounds.

In view of this, oats have been recognized worldwide as a highly valuable food product for maintaining a healthy lifestyle and a rational diet. In Ukraine, oats as a crop do not have a significant market value for most farmers, which is

confirmed by the low level of interest of commodity producers in its cultivation over a long period of time. However, in fact, oats have significant and still invaluable opportunities that are directly related to global trends in changing humanity's views on a healthy lifestyle and the development of organic agriculture, including poultry farming.

The analysis of scientific literature shows that the use of biologically active phenolic compounds of oats in the production of geese for meat can provide a number of potential benefits to the meat obtained. First, it is an increase in antioxidant activity. Phenolic compounds found in oats, such as ferulic acid, caffeic acid, and avenanthramides, are powerful antioxidants. These compounds help neutralize free radicals in the body, reducing oxidative stress and inflammation. The inclusion of oats in the geese diet can provide antioxidant protection, which will help improve the overall health of the bird and reduce the risk of oxidative damage to tissues, including muscle. Secondly, oat phenolic compounds have been shown to have anti-inflammatory properties, have a positive effect on animal development and, consequently, on the quality of the meat produced. Avenanthramides have a beneficial effect on the cardiovascular system, including lowering blood pressure and improving blood lipid profile. The inclusion of oats in the geese diet can help improve the condition of the cardiovascular system, which indirectly affects the quality of poultry meat. Thirdly, oat phenolic compounds reduce stress in animals. The inclusion of oats in the geese diet will help to reduce the negative impact of stress on the condition of the bird, which will also potentially lead to improved meat quality. Fourth, phenolic compounds improve the flavor profile of oats. Geese raised on a diet rich in oat phenolic compounds produce meat with improved flavor characteristics, which is also desirable for consumers. Fifth, natural preservation. Some phenolic compounds have antimicrobial properties that can help inhibit bacterial growth and extend the shelf life of meat products. Although the direct impact of oat phenolic compounds on meat preservation may be limited, their antioxidant and anti-inflammatory effects will indirectly contribute to the quality and shelf life of meat.

However, depending on the technological modes of oat use, the effect of its biologically active substances can vary significantly.

The aim of the research was to determine:

1. The content of avenanthramides in the green mass of sowing oats at the stage of milky-wax ripeness.

2. Influence of the technology of using green oat mass in feeding geese on their development and nutritional value of the resulting meat and its further oxidative deterioration during low-temperature storage.

8.2 Schemes and methods of research

8.2.1 Phenolic compounds of oats of the Spurt variety

The oats of Spurt variety were used in the research, the seeds of which were obtained from Synelnikov SDG ZG of Ukraine. The oats were grown on the black soil of the agricultural company "Victoria" of the Priazovsky district of Zaporizhzhia region.

The chromatographic analysis of phenolic compounds in oat samples was carried out by scientists from the Netherlands University, Department of Food Chemistry. For the extraction of phenolic compounds, the aerial part of oat *Avena sativa* L. was used in the earing and flowering phase. The extraction of flavonoids from the starting material was carried out with by methanol. The preliminary preparation of these oat samples included drying, grinding, and subsequent extraction of fats with hexane (**Fig. 8.1**) [12].

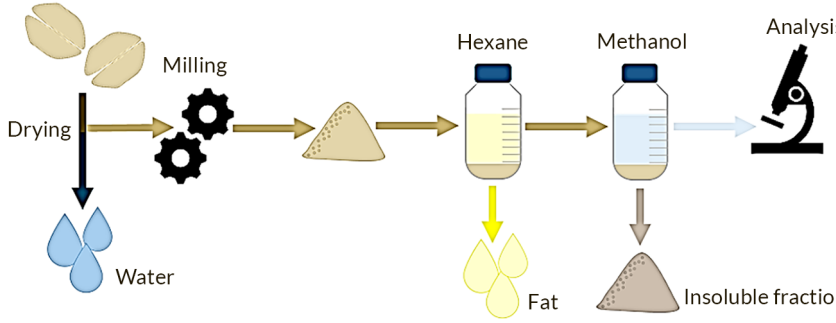

Fig. 8.1 Scheme of preparation of oat samples for chromatographic determination of phenolic compounds

8.2.2 Peculiarities of the influence of the technology of using oats in feeding geese on the poultry development and the quality of the meat obtained

The purpose of the first experiment was to determine the effect of the extract of *Avena sativa* L. on the antioxidant status and fatty acid composition of lipids in skeletal muscle of geese, dynamics of their live weight and pterilographic parameters during physiological stress formation of contour and juvenile feathers in this bird.

The study was conducted on Leghorn geese. At the age of 14 days, 2 groups of goslings (control and experimental) were formed on the principle of analogues, 26 birds each. Throughout the experiment, the birds of the control group were kept on a standard diet balanced in terms of metabolic energy, protein and vitamins according to recommendations [13]. Goslings of the experimental group were fed with oat extract from day 14 to day 49. For the extraction of biologically active compounds (BAS), the aerial part of oat *Avena sativa* L. was used in the earing and flowering phase. The extraction of phenolic compounds from the feedstock was carried out with water (ratio of feedstock to extractant – 1:10, extraction time in a boiling water bath – 60 min) followed by dilution of the extract 3 times. The object of study was the muscle tissue of geese limbs. Determination of the antioxidant activity and fatty acid composition of these tissues was carried out in physiologically reasonable terms: 14th day – completion of postnatal adaptation, 28th day – formation of contour feathers, 49th day – formation of juvenile feathers, 56th day – presence of formed plumage, stabilization of prooxidant-antioxidant balance [2]. The period of poultry keeping was determined by DSTU 3136-95 (8–9 weeks).

Geese were slaughtered and biological material for biochemical studies was collected weekly in compliance with the Council of Europe Convention for the Protection of Animals Used in Scientific Research (Strasbourg, 1986) and the First Scientific Congress of Ukraine on Bioethics (September, 2001).

The intensity of peroxidation processes was assessed by the content of its end products (TBARC) in tissue homogenates and by the initiation of lipid peroxidation (LPO) by Fe^{2+} (TBARCi) [14]. As an integral indicator of the state of the antioxidant defense system (AOS), the antioxidant activity coefficient (K_{AOA}) was used. It was calculated as the ratio of TBARC to TBARCi, since tissue homogenates contain not only the peroxidation substrate, but also components of the antioxidant defense system that can inhibit lipid peroxidation [15].

The fatty acid content was determined by gas-liquid chromatography, and lipid extracts for analysis were prepared according to the method of E. G. Bligh and W. J. Dyer with the recommendations of F. B. Palmer [16]. In addition to the total content of unsaturated fatty acids (SFA) (ΣC), the total equivalent concentration of SFA relative to multiple bonds (unsaturation, ΣN) was calculated [15]. In parallel, the dynamics of live weight of geese and their pterilographic parameters were monitored. Statistical processing of the results was performed using Microsoft Office Excel 2013 and SPSS v.13 with Student's t-test.

In the second experiment, a comparative analysis of the effect of oat extract and green oat mass on the antioxidant activity of geese muscle tissue in the

pre-slaughter period (from day 35 to day 63) and the nutritional value of the resulting meat was performed.

On the 35th day of postnatal goslings' development, 3 groups were formed (1 control and 2 experimental, 26 goslings in each). Geese in the control group were kept on a standard diet balanced in terms of metabolic energy, protein, and vitamins throughout the experiment according to recommendations [13]. The goslings of the I experimental group were supplemented with oat extract. Goslings of the II experimental group received an equivalent weight of the aerial part of milk-wax ripeness oats as part of the diet.

8.2.3 Analysis of the influence of oats on oxidative damage to meat

For the first experiment, we used goose meat from two samples. Meat of the control sample was obtained from geese of the control group, which were kept on a standard diet balanced in all nutrients. Meat of the experimental sample was obtained from geese of the experimental group, to the diet of which an aqueous extract of sowing oats was added from day 10 to day 50. Goslings were slaughtered at 60 days of age. After slaughtering, the goose carcasses were processed, frozen and then stored for 210 days at a temperature of –18 °C.

For the second experiment, two groups of 5 geese were formed. Geese of the control group received a standard diet, which included mixed fodder and grass mass, the basis of which was bird's foot (*Polygonum aviculare* L.). Geese in the experimental group received a similar diet, but 50 % of the grass mass was replaced with oats and alfalfa (25 % each). The addition of oats and alfalfa to the feed of geese in the experimental group lasted from day 7 to day 62. Geese were slaughtered on day 63. At this stage, the slaughter rates of geese were determined. After slaughtering, the geese carcasses underwent a number of technological procedures: exsanguination, scalding (70–75 °C), feather removal, removal of internal organs, washing, portioning and cooling (0–1 °C).

Goose meat from both groups were stored at –18 °C for 90 days. During this period, analytical measurements were made to determine meat quality indicators, including acidity, moisture content, protein, fat, moisture binding capacity, weight loss during defrosting, content of lipid peroxidation products, vitamins E, A, and β-carotene, fatty acid and amino acid composition. The above analyzes were performed on drumstick meat.

The moisture content of the meat samples was determined by the standard method, which includes the process of drying the samples in bunks [17].

The protein content was determined by the photocolorimetric method [18].

The content of intramuscular fat was determined by chloroform extraction using a Soxhlet apparatus. The method for determining moisture-binding capacity is based on the release of water from 300 mg of a sample during a 10-minute pressing with a 1 kg weight [17].

Vitamin E was analyzed by a spectrophotometric method based on the ability of vitamin E to reduce Fe^{3+} ions to Fe^{2+}. The resulting Fe^{2+} forms colored compounds upon interaction with 2.2-dipyridyl, which are identified and quantified [19].

For the analysis of vitamin A, we used its ability to form blue complex compounds when interacting with boron trifluoride ether ($C{\cdot}H{\cdot}OBF_{4103}$) [19].

The β-carotene content was determined by the color intensity of the extract by the photocolorimetric method. The color intensity was measured at a wavelength of 450 nm [19].

The study of amino acids was carried out on an automatic analyzer T 339 manufactured in the Czech Republic by ion-exchange liquid column chromatography [20].

8.3 Results and discussion

8.3.1 Phenolic compounds of oats

The results of chromatographic analysis of the methanolic extract of oat green mass and seeds confirmed the presence of avenanthramides in its composition (**Fig. 8.2**).

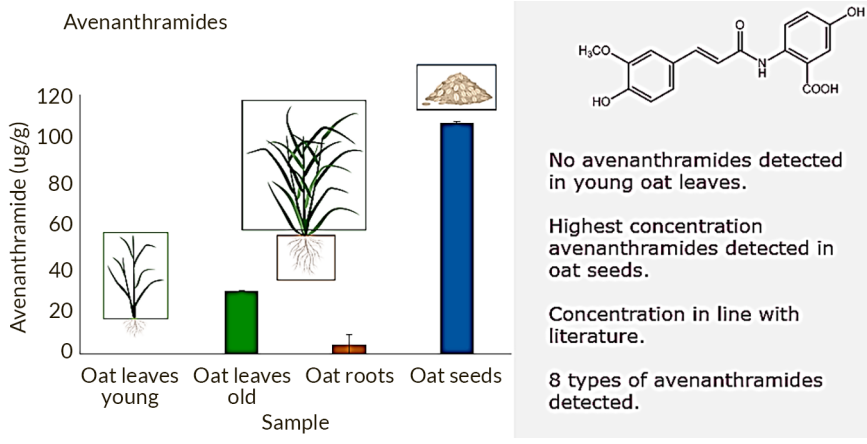

Fig. 8.2 Comparative analysis of avenanthramide content in oat plants and seeds

Comparative analysis of the green mass of oat and its seeds for the AVNs content shows that the content of these compounds in oat seeds is 3.72 times higher than in the aerial parts of plants. However, it should be borne in mind that the mass of oat greens in the geese diet is several times higher than the mass of oat seeds in the feed of this bird [11]. The presence of differin glycerol (DFG), an organic compound consisting of two molecules of ferulic acid esterified with a glycerol molecule, has been proven. This compound is a natural antioxidant and has antibacterial properties. In addition, it was found that oats also contain special phenolic compounds called oxylipins. The presence of 9 types of oxylipins in the studied oat samples was found, with the highest content in oat seeds (**Fig. 8.3**).

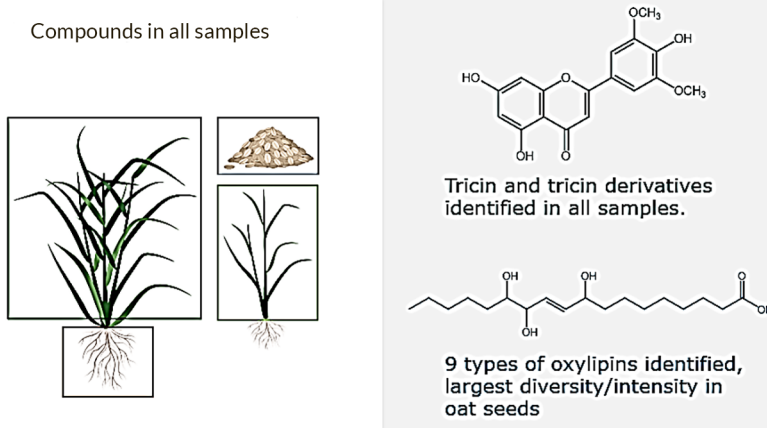

Fig. 8.3 The content of avenanthramides in oat plant parts and seeds

In humans, oxylipins play an important role in various processes, such as inflammatory and immune responses, apoptosis (programmed cell death), and regulation of hormone secretion. Some studies also point to possible beneficial properties of oxylipins for human health, including their antioxidant and anti-inflammatory effects [11]. The chromatogram of oat seeds shows the presence of tricine and its derivatives and oxylipins in addition to avenanthramides (**Fig. 8.4**).

In general, the results of the chromatographic analysis proved the presence of a number of compounds with powerful antioxidant properties not only in the grain, but also in the composition of the green mass of oats. Thus, the results of the chromatographic study confirmed the feasibility of using green oat mass in poultry feeding.

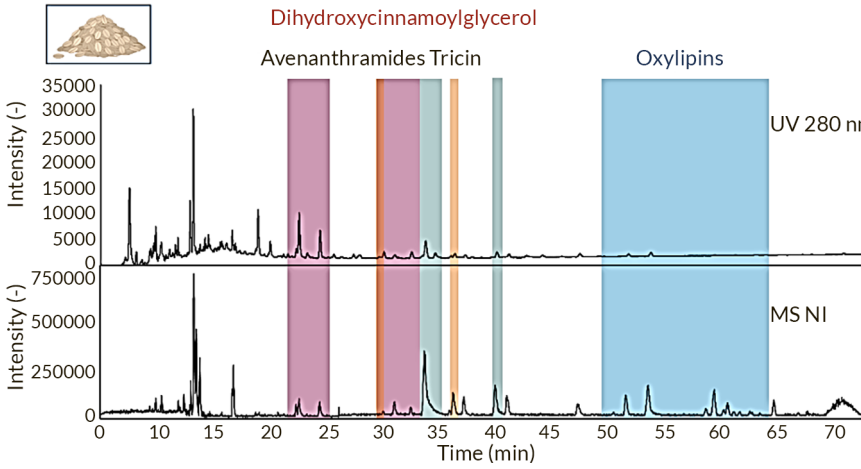

Fig. 8.4 Chromatogram of oat seeds

8.3.2 Peculiarities of the influence of oats in the geese diet on the development of the bird and the quality of the obtained meat

The formation of an adaptive response to the conditions of postnatal existence during the first two weeks of goslings' life is accompanied by an increase in the antioxidant status of their body [15]. The results of the experiment confirm a sufficiently high level of K_{AOA} in the studied tissues of 14-day-old goslings (**Table 8.1**).

From day 14 to day 28, contour feathers are formed, and a 29.4 % decrease in K_{AOA} is observed in the skeletal muscles of goslings of the control group. At the same time, under the influence of oat extract, the decrease in K_{AOA} in these tissues of goslings of the experimental group slows down (only by 25.0 %).

It is known that one of the mechanisms for improving the antioxidant status of tissues of a functioning organism during physiological stress may be a decrease in the content of the main substrate of lipid peroxidation, unsaturated fatty acids, and, accordingly, the ability of biomembrane lipids to oxidative damage [15–16]. The study of changes in fatty acid composition during the formation of contour and juvenile feathers helps to determine the mechanisms of increasing the adaptive status of geese at this period of ontogeny.

A comparative analysis of fatty acid composition (FAC) the muscle tissue of geese in the control group at 14 and 28 days of age shows some changes, but these

differences are insignificant compared to the difference in FAC of 28-day-old geese in the control and experimental groups (**Table 8.2**). First of all, a sharp drop in the total content of SFA under the influence of the extract is noteworthy. In the SM tissues of the experimental group, this indicator decreased by 3.6 times compared to the corresponding indicator of the control group.

The unsaturated fat content also decreases in SM by 2.3 times. Thus, the increase in antioxidant activity occurs both due to a reduction in the total content of PUFAs and metabolic processes aimed at reducing the content of polyunsaturated fatty acids (PUFAs), which is possibly realized by inhibiting fatty acid synthase [21] and blocking the expression of genes for other lipid metabolism enzyme.

Among all the differences in the unsaturated fatty acids in the SM tissues of 28-day-old geese, a sharp decrease (86.47 times) in the content of oleic acid under the influence of the extract is noteworthy. At the same time, a significant increase in saturated palmitic and stearic acids by 1.83–1.97 times was found in these tissues. Also, a significant decrease in the content of essential linoleic acid was found: under the influence of the extract in the SM tissues, its content decreased by 4.22 times. The content of the second essential linolenic acid decreased by 66.7 %. The content of essential arachidonic acid also significantly decreased (14.2 %), and the most unsaturated ω-3 docosahexaenoic acid disappeared under the influence of the extract.

Thus, the physiological stress in the body of geese associated with the formation of contour feathers under the influence of oat extract is significantly reduced due to the inclusion of regulatory mechanisms that selectively inhibit the synthesis of unsaturated fatty acids (UFA) [21]. This primarily concerns Δ-9 desaturase, which is involved in the synthesis of oleic acid. At the same time, elongases involved in the synthesis of palmitic and stearic acids are activated.

Further changes in FAC, accompanied by the formation of juvenile plumage in 49-day-old geese, are characterized by the FAC equalization of the control and experimental groups, first of all, an increase in the content of oleic acid in the SM of the experimental group to the level of the control group and, conversely, a decrease in the content of palmitic and stearic acids. The most significant differences in the tissues of 49-day-old goslings were found in ω-3 PUFA (linolenic by 41.2 % and docosahexaenoic by 2.33 times). Thus, the antioxidant effect of the extract is also manifested during the formation of juvenile plumage of a bird. However, the mechanism of realization of this effect at the stage of juvenile feather formation is different, which is confirmed by a decrease in the significant difference of the FAC of 49-day-old geese of the control and experimental groups.

Table 8.1 The coefficient of antioxidant activity of skeletal muscles of geese in ontogenesis and live weight of geese (*M*±*m*, *n*=6, experimental group – with oat extract in the geese diet)

	Fabric	Group	Age of geese, days			
			14	28	49	56
Antioxidant activity coefficient	Skeletal muscles	control	0.68	0.48	0.33	0.42
		experimental	0.68	0.51	0.45	0.53
Weight of geese, (M), kg		control	–	2.05±0.11	2.68±0.14	2.95±0.09
		experimental	–	2.12±0.08	2.91±0.10	3.36±0.13*

Table 8.2 Fatty acid content in skeletal muscles of geese in ontogenesis (*M*±*m*, *n*=6, experimental group – with oat extract in the geese diet)

Fatty acid	14	28		49		56	
	K	K	E	K	E	K	E
16:0	29.13±1.34	21.09±0.95	38.64±1.62**	24.71±1.63	22.93±0.96	20.94±0.87	21.70±1.03
18:0	18.13±0.93	21.94±1.03	43.28±1.94**	14.18±0.52	15.67±0.68	16.39±0.69	14.69±0.52
18:1	30.27±1.35	25.94±0.98	0.30±0.01**	38.24±1.67	37.27±1.43	33.71±1.05	39.53±1.73*
18:2	12.35±0.51	13.91±0.62	3.30±0.12**	11.11±0.36	12.78±0.47	11.94±0.42	11.30±0.38
18:3	0.15±0.01	0.09±0.00	0.15±0.00**	0.17±0.01	0.24±0.01**	0.19±0.00	0.26±0.01*
20:4	4.06±0.16	8.61±0.29	7.39±0.29*	5.56±0.21	4.70±0.19*	9.60±0.32	5.86±0.23**
22:3	0.09±0.00	0.19±0.05	0.21±0.01	0.14±0.00	0.17±0.00*	0.15±0.00	0.09±0.00**
22:4	–	0.20±0.01	–	0.29±0.01	0.29±0.01	0.32±0.01	0.11±0.00**
22:6	0.21±0.01	0.15±0.00	–	0.21±0.00	0.49±0.02**	0.43±0.02	0.29±0.01**
∑C NFA, %	50.61±1.93	52.83±2.07	14.61±0.63**	59.12±2.71	58.61±2.07	59.20±2.63	61.39±2.48
∑N	273.21	326.44	142.82	314.54	312.67	356.74	324.02

*Note: difference is significant relative to the control group: * – $p \leq 0.05$; ** – $p \leq 0.01$*

The stabilization of prooxidant-antioxidant balance in 56-day-old geese, which indicates the completion of feather formation processes, is characterized by a significantly higher content of ω-3 and ω-6 PUFAs in the SM of goslings of the experimental group.

Control of the dynamics of goslings' weight during the experiment shows a certain tendency to increase the weight of goslings of the experimental group compared to the control group (**Table 8.1**). However, the weight of geese of the experimental group compared to the control group (by 17.9 %) became significantly higher only at the end of the experiment at 56 days of age, which is an additional confirmation of the activation of the antioxidant defense system in geese under the influence of oat extract.

During the comparative analysis of the plumage condition in geese of the control and experimental groups at the end of the experiment (**Fig. 8.5**), it was found that in the control group the plumage of birds looks untidy, especially the forming wing feathers. The development of the feather cover is somewhat delayed, especially the primary and secondary feathers of the wing and rudder feathers compared to the contour feathers, in addition, the growth of feathers on the thighs and sides of the body is delayed.

Control group Experimental group

Fig. 8.5 Condition of wing feathers of geese of the experimental group at 56 days of age

In the experimental group, the plumage as a whole and on individual pteriles looks healthy and fresh. The flight and steering feathers on the back continue to grow. On other pterilia, the growth and development of feathers is complete, including down feathers and tassel feathers on the fifth point.

Thus, the addition of oat extract to the geese diet during feather formation increases the antioxidant activity of geese tissues. The increase in antioxidant activity in geese tissues not only contributes to a significant increase in the weight of geese at the end of the experiment, but also to the improvement of their pterilographic

indicators, which will also help reduce production costs, since geese feathers and down are a by-product that is in demand.

However, the technology with use of extract in poultry feeding involves additional costs for its production. In order to optimize the costs associated with the use of oat extracts, a comparative analysis of the effect of oat extract and its green mass in the geese diet in the pre-slaughter period (from 35 to 63 days) on the development of this bird and the quality of the meat obtained. This period of geese ontogeny is characterized by physiological stress in the bird's body (from day 42 to day 56) due to the formation of juvenile feathers. This process requires high energy and amino acids, including sulfur-containing ones. Therefore, even against the background of a diet balanced in terms of metabolic energy and protein, the process of juvenile feather formation is accompanied by tension in the antioxidant defense system [21].

A comparative analysis of the dynamics of TBAAP content in the muscle tissue of geese of the control and experimental groups shows (**Fig. 8.6**) that the addition of oat extract to the geese diet of the I experimental group, even for a week, contributes to a significant decrease in the TBAAP level in their muscle tissue (by 19.0 %, $p \leq 0.05$).

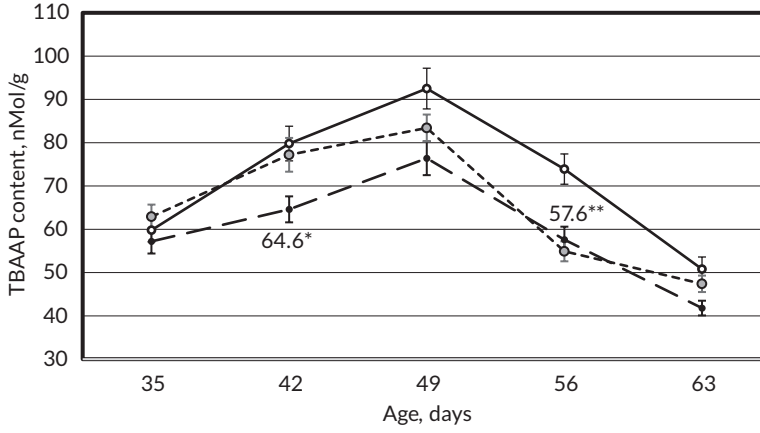

Fig. 8.6 Dynamics of TBAAP content in muscle tissue of geese of control (——), I experimental (— —) and II experimental (- - - -) groups, nMol/g ($M \pm m$, $n = 5$) (I experimental group – the oat extract, II experimental group – green mass of oat)

In 49-day-old goslings of the experimental group I, during the maximum stress of juvenile plumage formation and further until the end of the experiment, the content of these lipid peroxidation products remained significantly lower than the corresponding indicator of the control group of goslings (by 17.4–22.1 %, $p \leq 0.05$). Unlike oat extract,

the addition of its green mass to the diet of goslings of II experimental group at the beginning of the experiment did not cause significant changes in this indicator. However, in 49-day-old goslings of this group, against the background of the formation of juvenile plumage, a decrease in TBAAP content by 10.9 % ($p \leq 0.05$) was observed compared to the control. Later, in 56-day-old goslings, this difference increased to 25.7 %, but at the end of the experiment, the TBAAP content in the muscle tissue of geese of the control and II experimental groups probably did not differ (6.7 %).

The results of the correlation analysis of the TBAAP dynamics of the control and experimental groups of geese show that the addition of extract and green mass of oats to the geese diet does not significantly change the nature of the dynamics of this indicator in geese of both experimental groups compared to the control. This is confirmed by intergroup correlation coefficients of changes in TBAAP content (control and experimental groups): $r_1 = 0.950$ ($\gamma = 0.01$) and $r_2 = 0.863$ ($\gamma = 0.06$). Under the influence of oat extract, the average level of TBAAP in geese of the first experimental group decreased by 16.6 % compared to the control, and of the second experimental group – by 9.7 %, respectively.

The analysis of the results of this experiment shows that the positive effect of oats on the antioxidant activity of the geese SM is observed regardless of the technology of its use in poultry feeding [21]. During physiological stress, the formation of juvenile plumage in 49-day-old geese K_{AOA} muscle tissues of both experimental groups of geese significantly exceeded the corresponding indicator of the control group (by 62.5 and 34.4 %, respectively) (**Fig. 8.7**). The last two weeks of the experiment were characterized by a gradual restoration of prooxidant-antioxidant balance in the poultry body. However, even against the background of stabilization of the antioxidant defense system in 63-day-old geese, a significant increase in K_{AOA} of muscle tissues in the experimental groups compared to the control group was observed (by 32.7 and 25.0 %). The average level of K_{AOA} in the first experimental group exceeded the corresponding indicator of the control group by 27.9 %, and in the second experimental group – by 19.2 %.

The results of the correlation analysis of the dynamics of this indicator indicate that oat extract not only promotes more powerful activation of the antioxidant defense system of geese muscle tissue during the physiological stress of juvenile feather formation, but also significantly changes its nature: the correlation coefficient of the dynamics K_{AOA} of geese muscle tissue in the control and experimental groups $r = 0.570$. At the same time, the consistency of changes in this indicator of the control and II experimental groups was kept at a very close level ($r = 0.935$). Thus, the antioxidant effect of the oat aqueous extract is more significant, which is probably due to the better bioavailability of oat phenolic compounds in the extract.

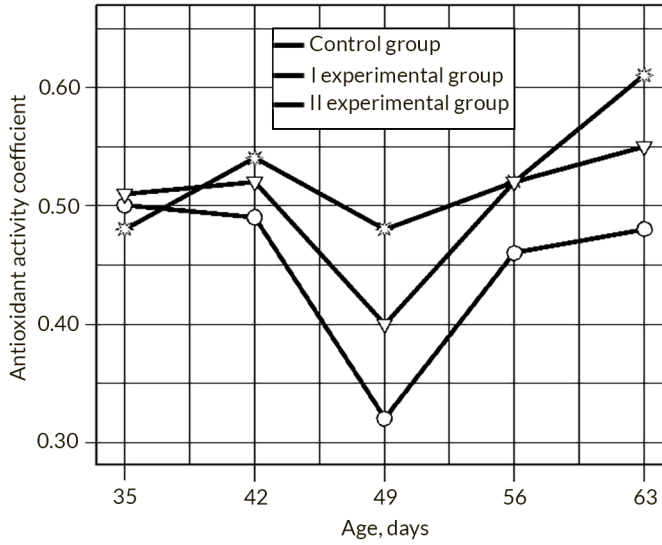

Fig. 8.7 Dynamics of the coefficient of antioxidant activity of skeletal muscles of geese (I experimental group – the oat extract, II experimental group – green mass of oat)

A comparative analysis of the fatty acid composition of lipids in the geese meat of the control and experimental groups after slaughter (63 days) shows that with the participation of oat BAC, there is a redistribution of fatty acids **(Fig. 8.8, 8.9**).

The general tendency to decrease the content of saturated fatty acids with a simultaneous increase in the level of unsaturated, including essential, fatty acids is noteworthy. Thus, the total content of saturated palmitic and stearic acids in the goose meat of the first experimental group decreased by 17.7 %, and the second experimental group – by 19.9 %, respectively, while the content of essential linoleic and linolenic acids significantly increased in the meat of the I group of geese, and essential arachidonic acid – in the meat of the II group. As a result, it was in the meat of the II experimental group that a greater increase in ω3- and ω6-polyunsaturated fatty acids (PUFAs) was found.

Thus, under both technological modes of application of oat BAC in feeding geese, an increase in the antioxidant activity of muscle tissue and, accordingly, the activity of endogenous antioxidants in meat obtained after slaughter was found. However, the differences in the FAC of lipids in the meat of the experimental groups of geese prove the existence of differences in the mechanisms of antioxidant effects. Further research should be aimed at optimizing the technological

modes of application of oat bioactive substances in order to obtain goose meat of higher quality.

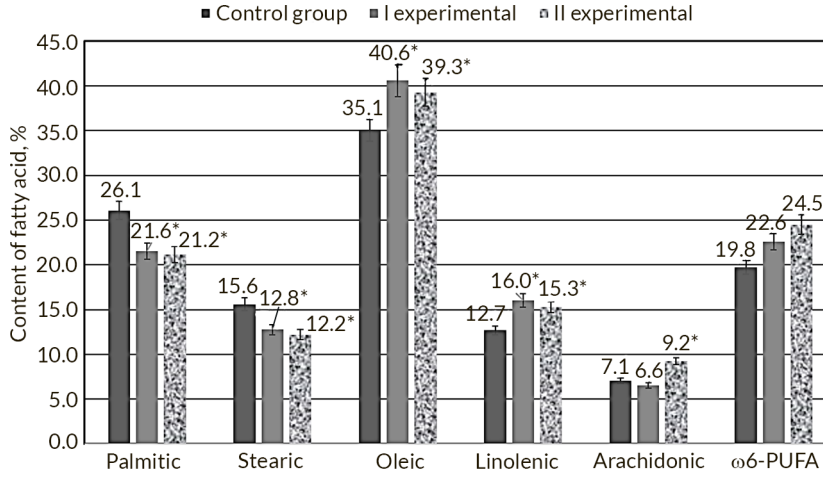

Fig. 8.8 The content of fatty acids in geese meat after slaughter ($M \pm m$, $n=6$) (I experimental group – the oat extract, II experimental group – green mass of oat)

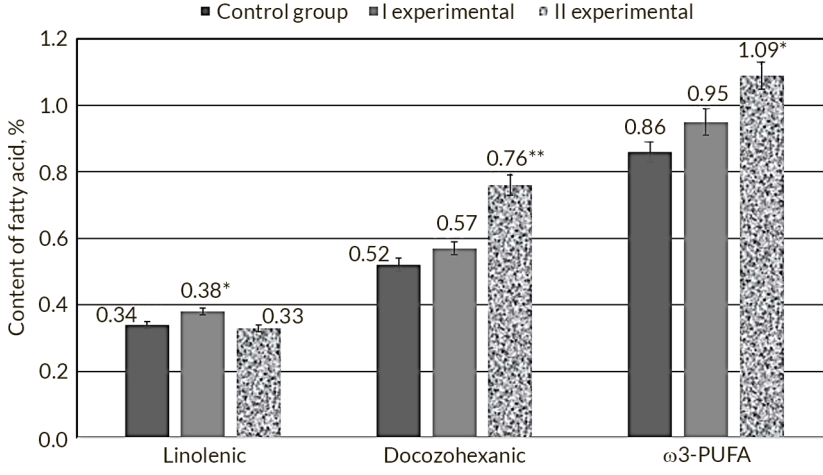

Fig. 8.9 The content of fatty acids in geese meat after slaughter ($M \pm m$, $n=6$) (I experimental group – the oat extract, II experimental group – green mass of oat)

8.3.3 Peculiarities of influence of oats and alfalfa in feeding geese on the quality of the obtained meat

This section presents the results of a study of the influence of aqueous extract of oats and a mixture of oats and alfalfa in the geese diet on the quality of meat during storage.

The live weight of geese before slaughter in the experimental group treated with oat extract was 11.3 % higher ($p<0.05$) compared to the control group (**Table 8.3**). The weight of the gutted carcass of the experimental group was also higher by 11.8 % ($p<0.05$) compared to the control group. The muscle weight of geese of the experimental group exceeded that of the control group by 12.4 % ($p<0.05$). An increase in breast and leg weight was also noted by 21.2 % and 11.7 %, respectively ($p<0.05$).

Table 8.3 Geese meat yield ($M\pm m$, $n=6$, experimental group – with oat extract in the geese diet)

Indicator	Control group	Experimental group
Live weight before slaughter, g	3215.0±86.8	3567.3±157.0*
Weight of gutted carcass, g	1802.0±75.7	2014.7±70.5*
Output of gutted carcass, %	56.1±1.7	56.5±1.7
Muscle mass, g	949.7±37.0	1067.4±42.7*
Meatiness index, %	29.5±0.8	29.9±1.0
Weight of edible parts, g	1643.8±70.7	1749.8±64.7
Edible parts index, %	51.1±1.8	49.1±1.4
Breast weight, g	202.4±5.3	245.3±8.3*
Weight of the lower legs, g	209.8±8.0	234.4±10.5*

The addition of a mixture of oats and alfalfa contributed to an increase in live weight of geese in the experimental group by 11.5 % ($p\leq0.05$). An increase in the weight of gutted carcasses of geese of the experimental group by 17.1 % was recorded compared to the corresponding indicator of the control group (**Table 8.4**).

The advantage in the weight of muscle tissue in geese of the experimental group was found to be 18.3 %. The introduction of oats and alfalfa into the diet caused an increase in the weight of edible parts by 12.1 % ($p\leq0.05$). There was also a significant increase in the weight of the thoracic muscle part and legs by 26.4 % and 24.5 %.

The positive impact on meat yield may be due to the presence of phenolic compounds in oats and alfalfa, which play a key role in improving the growth characteristics of animals. These substances can stimulate the secretion of digestive enzymes,

minimize the presence of pathogenic microflora in the gastrointestinal tract and improve intestinal morphology. A a result of this biochemical interaction, nutrient absorption is more efficient, which contributes to the increase in animal weight [22].

Table 8.4 Geese meat yield ($M \pm m$, $n = 6$, experimental group – with oat and alfalfa grass in the geese diet)

Indicator	Control group	Experimental group
Live weight before slaughter, g	3697.8±81.1	4124.4±115.6*
Weight of gutted carcass, g	2100.0±82.4	2458.2±97.3*
Output of gutted carcass, %	56.7±1.0	59.5±0.7
Muscle mass, g	1151.6±37.6	1362.2±32.7**
Meatiness index, %	31.1±0.3	33.0±0.4*
Weight of edible parts, g	1705.4±48.9	1910.4±58.2*
Edible parts index, %	46.1±0.4	46.3±0.4
Breast weight	248.6±12.3	314.2±7.8**
Weight of the lower legs	214.0±9.3	266.4±9.2*

Analysis of the moisture content of the meat of the control group showed that during the specified shelf life, this indicator decreased by 9.2 %. In the meat of the experimental group, which was obtained with the use of oat extract, the decrease in moisture content was 8 % (**Fig. 8.10**).

The research results of the effect of oat and alfalfa grass on goose meat revealed a decrease in moisture levels in samples from both groups (**Fig. 8.11**).

After a shelf life of 90 days, a 7.8 % decrease in moisture content ($p \leq 0.01$) was found in the geese meat of the control group. Similar dynamics of moisture reduction was recorded for the goose meat of the experimental group. In the goose meat of the experimental group, a higher protein content was found by 5.0 % ($p \leq 0.05$). The level of intramuscular fat remained at the same level in the meat of both groups throughout the entire storage period.

A gradual decrease in moisture and protein content in meat during storage at low temperatures is possible due to the formation of ice crystals in the intercellular space and changes in the concentration of dissolved substances in water that does not become solid. These phenomena can lead to the destruction and oxidation of protein structures, which affects the ability of meat to retain water. The freezing process causes denaturation of myofibrillar proteins, including changes in their secondary and tertiary structure due to cold denaturation. Activation of cellular enzymes is also observed, which accelerates the processes of protein degradation and oxidation [23].

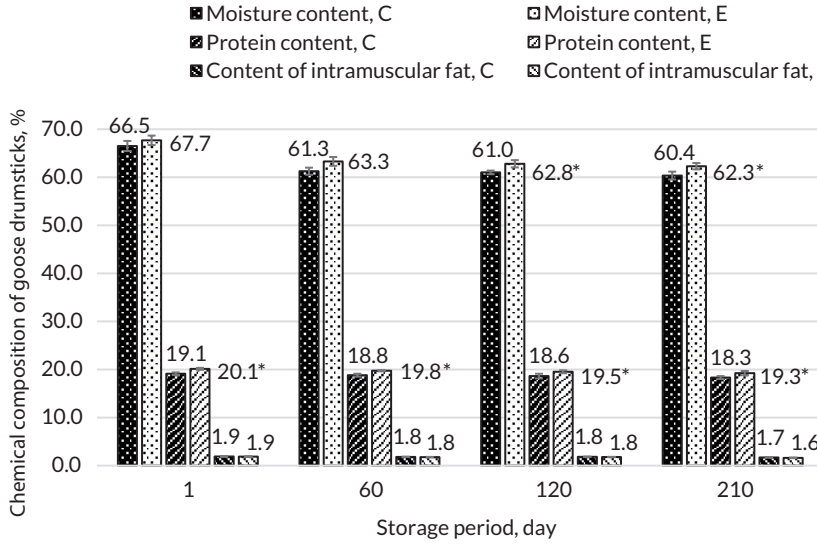

Fig. 8.10 Chemical composition of the goose meat thighs ($M \pm m$, $n = 3$, experimental group – with oat extract in the geese diet)

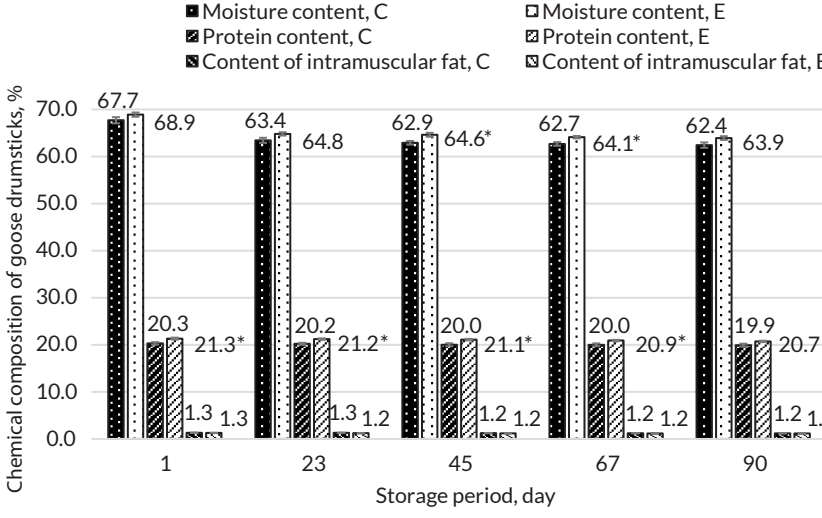

Fig. 8.11 Chemical composition of the goose meat thighs ($M \pm m$, $n = 5$, experimental group – with oat and alfalfa grass in the geese diet)

On the other hand, alfalfa as a source of protein and amino acids helps to increase the protein content in the muscle tissue of geese. The use of alfalfa silage in the diet enriches the diet with amino acids and biologically active components. This improves metabolic processes, increases the efficiency of digestion and absorption of nutrients, reduces the accumulation of fat deposits and increases the amount of muscle mass [24].

Insignificant fluctuations in pH were recorded in the meat of the control and experimental groups, to the diet of which oat extract was added (**Table 8.5**). The moisture binding capacity (MBC) of meat was higher in the experimental group during the entire storage period. The largest difference in this indicator for the control and experimental groups was found on the 60th and 210th day of storage and amounted to 10.2 % and 10.4 % ($p \leq 0.05$), respectively.

Table 8.5 Indicators of geese meat during storage ($M \pm m$, $n = 6$, experimental group – with oat extract in the geese diet)

Shelf life of days	pH		Weight loss during defrosting, %		GWP, %	
	K	E	K	E	K	E
1	6.04±0.01	6.03±0.01	–	–	87.1±3.27	87.6±2.99
60	6.01±0.01	6.01±0.01	3.57±0.05	3.55±0.05	72.2±2.16	79.5±1.55*
120	5.98±0.02	5.99±0.03	3.60±0.07	3.57±0.08	68.5±1.12	73.9±2.45
210	5.94±0.02	5.96±0.03	3.64±0.08	3.58±0.08*	66.4±1.13	73.3±1.57*

In the experiment, with the addition of oats and alfalfa to the geese diet, a decrease in the acidity of meat for both groups of geese was found during 90 days of low-temperature storage (**Table 8.6**). The moisture-binding capacity of meat in the control group decreased by 17.7 % after 90 days of storage, while in the experimental group a decrease of 14.4 % was observed. On the 45th and 67th day of storage in the experimental group, the moisture content of meat was higher by 6.1 % and 7.3 % ($p \leq 0.05$), respectively. An increase in meat weight loss during its defrosting was found with an increase in the shelf life. However, in the experimental samples, weight loss was lower at all stages of storage. The largest difference was recorded on the 45th day of storage, when the mass loss in the experimental group was 8.3 % lower ($p \leq 0.05$).

The increase in moisture-binding capacity in the meat of the experimental group is possible due to an increase in the amount of hydrophilic proteins that contribute to water retention in meat tissues. Among these proteins, myosin and other sarcoplasmic components play a crucial role in moisture retention. They ensure less water

loss during the cryopreservation process and subsequent thawing. The freezing process converts water in meat into ice crystals, which can cause mechanical damage to meat fibers and lead to dehydration during thawing. However, the increased moisture-binding capacity of meat can help minimize structural damage to meat fibers, significantly reducing water and weight loss during defrosting.

Table 8.6 Indicators of geese meat during storage ($M \pm m$, $n = 6$, experimental group – with oat and alfalfa grass in the geese diet)

Shelf life of days	pH		Weight loss during defrosting, %		GWP, %	
	K	E	K	E	K	E
0	6.15±0.01	6.14±0.01	–	–	91.4±1.01	93.2±1.10
23	6.14±0.01	6.14±0.01	2.74±0.08	2.54±0.07	81.0±1.43	85.8±0.59*
45	6.12±0.01	6.13±0.01	3.09±0.05	2.83±0.07*	77.5±1.05	82.2±0.63*
67	6.12±0.01	6.13±0.01	3.14±0.05	2.92±0.05*	75.0±1.40	80.5±0.84*
90	6.11±0.01	6.12±0.01	3.28±0.05	3.05±0.07*	75.2±1.61	79.8±1.34

During the first 60 days of storage in the meat of the control group, there was a gradual decrease in lipid peroxidation products (LPO), reaching a minimum level that was 2.6 times lower than the initial value. The further intensification of LPO processes in the control meat sample was due to the accumulation of endogenous oxygen during storage. A particularly pronounced increase in the activity of lipid peroxidation was recorded starting from the fourth month of storage, which led to a significant increase in the content of secondary lipoperoxidation products – 8.2 times after 210 days of storage compared to the initial value.

The goose meat from the experimental group was characterized by 83.8 % higher TBAAP levels than the meat of the control group (**Fig. 8.12**). The inclusion of oat extract in the geese diet contributed to the preservation of the stability of the prooxidant-antioxidant balance in the meat of the experimental sample. During the first 60 days of storage, the content of lipoperoxidation end products remained stable. With further storage from the 60th to the 120th day, a 3.7-fold decrease in this indicator was observed, and from the 120th to the 210th day, activation of lipid peroxidation began, which led to a 10.7-fold increase in TBAAP levels. In general, during the entire storage period, the content of secondary lipoperoxidation products in the meat of the experimental sample increased by 3.2 times, but at the end of storage it was 28.6 % lower than that of the control group.

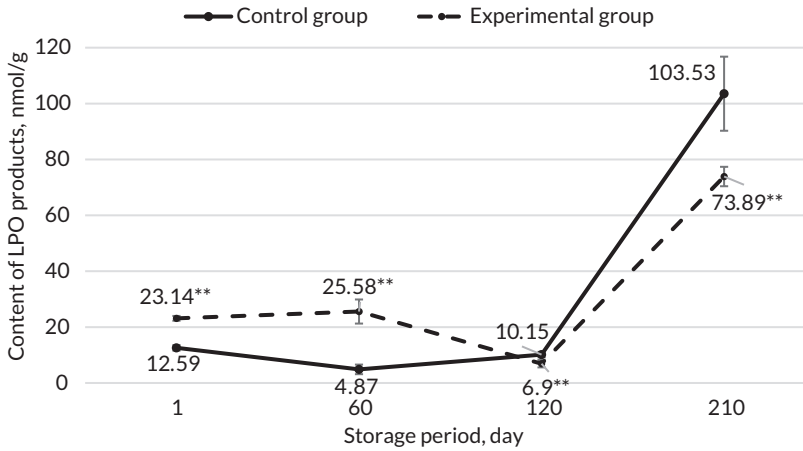

Fig. 8.12 Dynamics of the TBAAP content in the goose meat thighs ($M \pm m$, $n = 3$, experimental group – with oat extract in the geese diet)

In the second experiment, when studying the effect of oat and alfalfa grass on goose meat, the analysis of the content of LPO products in the goose meat of the control group showed that during the first 23 days of storage this indicator remained unchanged (**Fig. 8.13**). Starting from the 23rd day, an activation of oxidative processes was observed, which led to an increase in the TBAAP level by 18.3 % on the 45th day of storage. From the 45th to the 67th day, there was a further increase in the concentration of LPO products by 38.7 %. After that, by the end of the storage period, the level of lipid peroxidation products in the meat of the control group stabilized.

The meat of the experimental group was characterized by a lower content of lipid peroxidation products by 8.9 % ($p \leq 0.05$) compared to the control group. In addition, it showed a prolongation of the period of stability of prooxidant-antioxidant equilibrium, where the accumulation of LPO products was slower. By the 45th day of storage, the difference in TBAAP content between the control and experimental groups increased to 13.9 % ($p \leq 0.01$), and by the 67th day – to 28.3 % ($p \leq 0.01$). However, after the 67th day of storage, an acceleration of the LPO processes was observed in the experimental samples, and by the 90th day the content of LPO products increased by 35.8 % ($p \leq 0.01$).

The inclusion of oats and alfalfa in the geese diet helps to prolong the period of stabilization of prooxidant-antioxidant balance during meat storage [25]. It is known that the antioxidant potential and quality of nutrients entering the animal's body is determined by the diet composition and the BAS bioavailability [26]. The change

in the amount of ROS products in the goose meat of the experimental group is probably the result of the action of avenanthramides, polyphenols, flavonoids, and other bioactive substances contained in oats and alfalfa. Such changes contribute to optimizing the biochemical composition and increasing the biological value of meat [26].

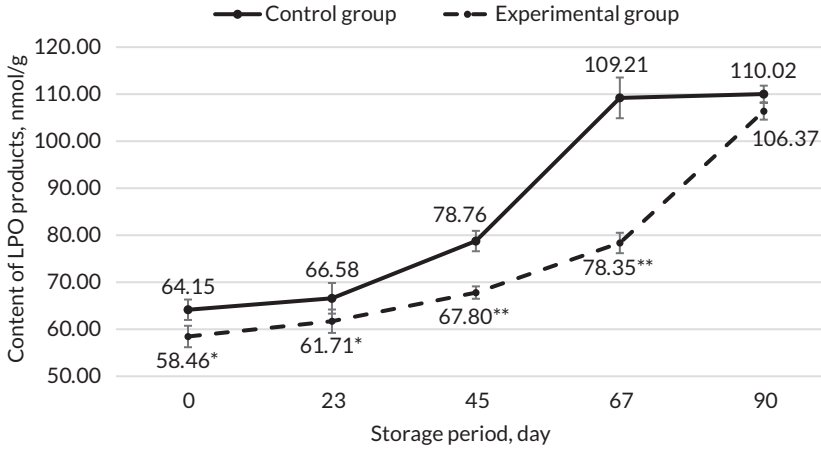

Fig. 8.13 Dynamics of the TBAAP content in the goose meat thighs ($M \pm m$, $n = 5$, experimental group – with oat and alfalfa grass in the geese diet)

This is confirmed by the detected changes in the dynamics of TBAAP indicators, which indicates an improvement in the stability of the fatty component of meat throughout the entire storage period. Thus, the established changes in the dynamics of TBAAP indicate that the addition of oats and alfalfa to the geese diet has a positive effect on the stability of the lipid component of meat throughout the entire shelf life [27].

Depending on the initial state of chickens and the technological conditions of their keeping, the fatty acid composition of poultry meat lipids can change significantly [28, 29]. The analysis of the fatty acid composition of the goose meat of the first experiment shows that among the unsaturated fatty acids in the meat of the control group, the highest content is oleic, linoleic, and arachidonic acids, and among the saturated ones, palmitic and stearic acids (**Table 8.7**). During the first 120 days of storage, the total share of PUFAs in the goose meat of the control group increased by 11.7 % due to oleic (23.9 %), linoleic (13.6 %) and linolenic (2.22 times) acids. A significant decrease in the content of the most unsaturated docosahexaenoic acid (by 2.57 times) compensated for a more significant increase in the level of unsaturated fatty acids during this period. The second part of the experiment was characterized

by significant losses of the most unsaturated fatty acids: arachidonic (by 42.9 %) and docosahexaenoic (by 34.8 %). At the same time, the content of essential linoleic and linolenic acids increased significantly (by 47.1 % and 2.65 times, respectively).

Table 8.7 Dynamics of the content (ω, %) of fatty acids in geese meat during storage ($M \pm m$, $n = 3$, experimental group – with oat extract in the geese diet)

Fatty acid	Shelf life, days					
	1		120		210	
	K	E	K	E	K	E
(16:0)	19.48±0.51	20.74±0.79	19.05±0.65	20.92±0.77*	20.09±0.7	20.99±0.92
(18:0)	22.31±0.89	18.61±0.8**	17.9±0.55	18.24±0.51	15.7±0.53	16.07±0.53
(18:1)	27.84±0.84	30.49±0.76	34.48±1.55	27.3±0.93*	32.12±0.84	35.56±1.42*
(18:2) ω6	14.7±0.66	16.25±0.73*	16.74±0.54	18.99±0.85*	24.56±1.11	17.41±0.5*
(18:3) ω3	0.09±0.01	0.13±0.01**	0.2±0.01	0.15±0.01*	0.53±0.02	0.29±0.01**
(20:4) ω6	6.04±0.25	6.64±0.23*	5.63±0.23	7.47±0.28**	3.19±0.13	5.12±0.18**
(22:6) ω3	0.59±0.02	0.55±0.02	0.23±0.01	0.62±0.02**	0.15±0.01	0.17±0.01
SFA	45.56±1.54	42.65±1.68	39.57±1.29	42.26±1.39	37.48±1.29	39.24±1.52
UFA	53.81±1.93	57.15±1.86	60.14±2.43	57.39±2.21	62.29±2.16	60.61±2.19
MUFA	31.27±0.95	32.59±0.84	36.42±1.62	29.17±1.01	33.79±0.9	37.25±1.48
PUFA	22.54±0.98	24.56±1.02	23.72±0.81	28.22±1.2**	28.5±1.26	23.36±0.71*
ω3-PUFA	0.68±0.02	0.68±0.02	0.43±0.02	0.77±0.03**	0.68±0.02	0.45±0.02**
ω6-PUFA	20.74±0.92	22.89±0.96*	22.38±0.77	26.46±1.14*	27.75±1.23	22.53±0.68*

These oppositely directed changes in the FAC of meat of the control group resulted in stabilization of both total unsaturation and total PUFA content during this experimental period. The results of the comparative analysis of the fatty acid composition of the meat of the control and experimental samples at the beginning of the experiment confirm the positive effect of oat extract on the fatty acid composition of goose meat. Before being stored, the experimental sample of meat exceeded the control sample in terms of oleic (by 9.5 %) and essential linoleic (by 10.5 %), linolenic (by 44.4 %) and arachidonic acids (by 9.9 %). In terms of the total content of NFAs and their unsaturation, the experimental sample exceeded the control sample less significantly (by 6.2 % and 6.9 %, respectively, $p \leq 0.05$). After 120 days of storage, the meat of the experimental sample contained 13.8 % more linoleic acid, 33.9 % more arachidonic acid, and 2.70 times more docosahexaenoic acid compared to the corresponding control meat sample. In terms of total unsaturation of FA, the experimental

sample significantly (by 6.3 %, $p \leq 0.05$) exceeded the control sample. Thus, the positive effect of oat extract on the fatty acid content of geese meat was observed during 120 days of storage. In the second part of the experiment, the changes in the quality of the meat of the experimental sample were less positive. After 210 days of storage, the experimental sample had a significantly higher content of the most abundant unsaturated oleic acid (by 10.7 %), arachidonic acid (by 59.4 %), and docosahexaenoic acid (by 13.3 %). However, the content of linoleic and linolenic acids was lower than that of the control sample (by 29.1 % and 45.3 %, respectively).

The analysis of the goose meat FAC after slaughtering the birds of the second experiment revealed that as a result of the use of oats and alfalfa (**Table 8.8**), the content of oleic acid in the meat of the experimental sample decreased by 9.7 % ($p \leq 0.05$). At the same time, an increase in the content of polyunsaturated fatty acids, namely linoleic and linolenic acids, was recorded by 19.1 % ($p \leq 0.01$) and 32.0 % ($p \leq 0.01$), respectively. In addition, a significant increase in the level of docosahexaenoic acid (by 20.6 %) was found. There was also an increase in the total content of ω3- and ω6-polyunsaturated fatty acids in the meat of the experimental samples by 24.2 % ($p \leq 0.01$) and 10.8 % ($p \leq 0.05$), respectively.

Table 8.8 Dynamics of fatty acid content in geese meat during storage (ω, %, $M \pm m$, $n = 3$, experimental group – with oat and alfalfa grass in the geese diet)

Fatty acid	Shelf life, days			
	1		90	
	Control	Experiment	Control	Experiment
(16:0)	21.78±0.72	21.91±0.9	20.66±0.81	20.86±0.73
(18:0)	14.3±0.4	14.97±0.66	15.73±0.77	13.43±0.48**
(18:1)	35.39±1.34	31.96±1.05*	32.87±1.02	33.68±0.98
(18:2) ω6	13.95±0.5	16.61±0.6**	17.1±0.75	17.94±0.77
(18:3) ω3	0.26±0.01	0.34±0.01**	0.35±0.01	0.47±0.02**
(20:4) ω6	8.1±0.32	7.81±0.22	6.9±0.28	6.49±0.19
(22:6) ω3	0.55±0.02	0.66±0.03**	0.62±0.02	0.96±0.04**
SFA	38.57±1.21	39.65±1.66	39.11±1.38	36.64±1.29
UFA	61.05±2.31	59.78±1.99	60.52±2.18	62.77±2.12
MUFA	37.9±1.45	33.95±1.12	35.02±1.1	36.05±1.05
PUFA	23.15±0.87	25.84±0.87*	25.49±1.08	26.72±1.07
ω3-PUFA	0.81±0.03	1.01±0.04**	0.97±0.03	1.42±0.06**
ω6-PUFA	22.05±0.83	24.42±0.82*	24.0±1.03	24.73±0.98

After 90 days of low-temperature storage, an increase in the content of linoleic and linolenic acids by 22.6 % and 34.6 % ($p \leq 0.01$), respectively, was observed in the goose meat of the control group. A decrease in the level of arachidonic acid by 14.8 % ($p \leq 0.01$) was detected. In the sample of meat of the experimental group, the content of linolenic and docosahexaenoic acids exceeded the value of the meat of the control group by 32.3 % and 53.8 %, respectively. There was also a tendency to a decrease in the content of saturated fatty acids and an increase in the content of polyunsaturated fatty acids. The content of ω3-polyunsaturated fatty acids in the experimental group was 46.4 % higher than that of the control group.

The recorded improvement in the fatty acid profile of meat in the experimental group can be explained by the influence of antioxidants, in particular those contained in oats. After all, oats have been shown to be rich in antioxidants such as β-glucan, avenanthramides, polyphenols, flavonoids, and β-carotene [5]. These substances play a key role in protecting lipids from oxidation, contributing to the preservation of unsaturated fatty acids in meat [10].

Such changes may also be due to the high levels of linoleic and linolenic acids present in oats and alfalfa [10]. These acids can be assimilated by the body of geese, which contributes to the optimization of the fatty acid content of the goose meat in the experimental group [30]. An increase in the proportion of ω3-PUFA may be caused too by the preservation of a certain activity of the corresponding desaturases [31].

The addition of oats and alfalfa to the geese diet had a positive effect on the vitamin composition of the meat obtained (**Fig. 8.14**). A significant increase in the content of vitamin E by 38.5 % and β-carotene by 19.6 % ($p \leq 0.01$) was found in the goose meat of the experimental group.

After 90 days of low-temperature storage, a decrease in the content of vitamin A and β-carotene in the meat from the control group was observed by 33.6 % and 64.2 %, respectively. A decrease in vitamin E content by 12.3 % ($p \leq 0.05$) was also recorded.

On the other hand, in the meat of the experimental group on the 90th day of storage, the vitamin E content exceeded that of the control group by 50.9 %. In addition, the experimental sample showed a 20 % higher content of β-carotene ($p \leq 0.01$). The study found no significant effect of oats and alfalfa on the vitamin A content of goose meat. The changes in the content of vitamin E and β-carotene may be based on their high content in oats, which could be incorporated into the poultry body [10]. Also, a decrease in the intensity of oxidative processes in meat may be caused by the action of bioactive elements present in oats that have antioxidant activity. Among these components, a special place is occupied by avenanthramides [32]. The reason for the decrease in the amount of β-carotene during storage is its oxidation, which can occur

by enzymatic and non-enzymatic means [33]. The decrease in the level of vitamin E can be explained by its antioxidant activity and, accordingly, the ability to protect meat lipids from oxidation [10]. However, its insignificant loss is evidence of the implementation of other mechanisms of antioxidant protection in the meat of the control sample.

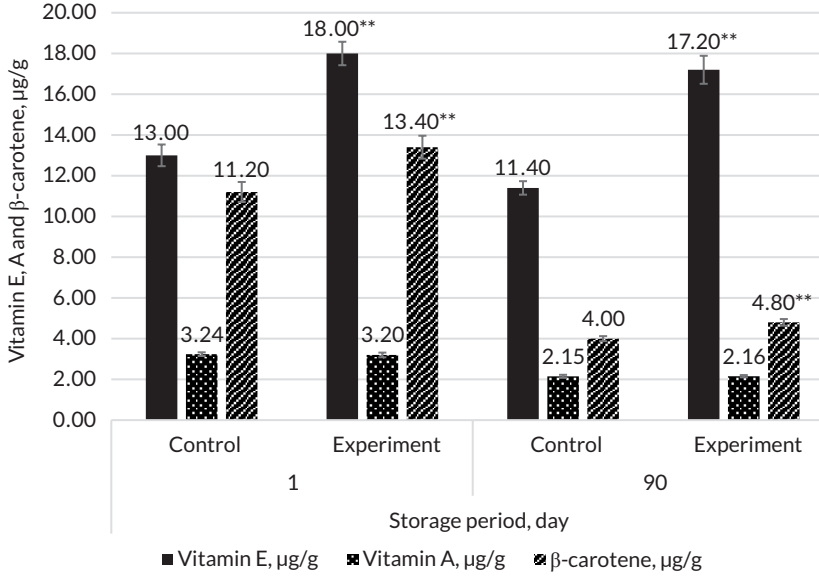

Fig. 8.14 Dynamics of the content of vitamins A, E and β-carotene (μg/g) in the goose meat ($M \pm m$, $n = 5$, experimental group – with oat and alfalfa grass in the geese diet)

The analysis of changes in the amino acid composition of goose meat (**Table 8.9**) indicates an increase in the content of essential amino acids in the goose meat of the experimental group.

This was observed not only immediately after slaughter, but also after 90 days of low-temperature storage. An increase in threonine and methionine by 26 % and 22.8 %, respectively ($p \leq 0.01$) was detected.

After 90 days of storage, a decrease in the content of threonine and methionine was observed in the meat of both groups. In addition, a decrease in the amount of phenylalanine was detected in the test sample. At the same time, an increase in the level of valine was noted in both study groups, and an increase in isoleucine was also recorded in the samples of the experimental group. Against the background of the use of oats and alfalfa in the geese diet, a statistically significant increase in the

content of lysine (by 13.4 %), valine (by 23.7 %), isoleucine (by 26.3 %), leucine (by 17.7 %) was recorded on the 90th day of storage of meat of the experimental group compared to the control group. At the same time, a 21 % decrease in threonine and a 49 % decrease in phenylalanine was found.

Table 8.9 Dynamics of amino acid content in goose meat during storage (mg/100 g, $M \pm m$, $n = 3$, experimental group – with oat and alfalfa grass in the geese diet)

Amino acid	Shelf life, days			
	1		90	
	Control	Experiment	Control	Experiment
Lysine	2.00±0.1	2.09±0.1	2.11±0.11	2.39±0.12**
Histidine	0.56±0.03	0.62±0.03*	0.31±0.02	0.25±0.01**
Arginine	1.59±0.08	1.61±0.08	1.26±0.06	1.22±0.06
O-proline	1.31±0.07	0.99±0.05**	0.88±0.04	0.58±0.03**
Aspartic acid	1.11±0.06	1.21±0.06*	1.63±0.08	1.41±0.07*
Threonine	0.72±0.04	0.91±0.05**	0.26±0.01	0.21±0.01**
Serine	0.64±0.03	0.79±0.04**	0.39±0.02	0.32±0.02**
Glutamic acid	2.94±0.15	3.17±0.16	3.56±0.18	3.54±0.18
Proline	0.94±0.05	0.81±0.04*	0.84±0.04	1.00±0.05**
Glycine	0.90±0.04	0.98±0.05*	1.03±0.05	1.16±0.06*
Alanine	1.19±0.06	1.29±0.06	1.67±0.08	1.76±0.09
Cystine	0.46±0.02	0.51±0.03*	0.33±0.02	0.32±0.02
Valine	0.83±0.04	0.91±0.05*	0.98±0.05	1.22±0.06**
Methionine	0.29±0.01	0.35±0.02**	0.16±0.01	0.15±0.01
Isoleucine	1.08±0.05	1.10±0.06	1.11±0.06	1.40±0.07**
Leucine	1.89±0.09	1.94±0.1	2.14±0.11	2.52±0.13**
Tyrosine	0.48±0.02	0.61±0.03**	0.35±0.02	0.27±0.01**
Phenylalanine	0.90±0.05	0.91±0.05	0.91±0.05	0.46±0.02**

The reason for the changes in the amino acid composition of meat may be the presence of oats and alfalfa in the diet. The addition of alfalfa has been shown to increase protein content, reduce cholesterol and fat, and improve the antioxidant status of chicken meat [7]. Oats contain high levels of threonine, methionine and other essential amino acids, which may also contribute to their increase in geese meat [34].

Conclusions

The results of the chromatographic analysis proved the presence of compounds with powerful antioxidant properties of avenanthramides of 8 types not only in the grain, but also in the composition of green oat mass and, thus, confirmed the feasibility of using green oat in poultry feed.

With both technological regimes of using oats in feeding geese (green oat mass or its extract), an increase in the antioxidant activity of muscle tissue and, accordingly, the activity of endogenous antioxidants in meat obtained after slaughter was observed. However, the addition of green oat to the geese diet of experimental group II led to a significantly greater increase in the content of ω3- and ω6-polyunsaturated fatty acids compared to the control after slaughter.

Addition of oat extract to the geese diet led to an increase in the time of pro-oxidant-antioxidant balance in meat during storage. An increase in the content of essential fatty acids was found in the meat of this experimental group. After 120 days of storage, the content of linoleic, arachidonic, and docosahexaenoic acids was higher in the meat of the experimental group. After 210 days of storage, an increase in the content of oleic, arachidonic and docosahexaenoic acids was observed in the meat of the experimental group compared to the control group. However, in terms of the content of linoleic and linolenic acids, the experimental sample yielded to the control.

Incorporating a mixture of oats and alfalfa into the geese diet leads to an 11.5 % increase in live weight, indicating the high effectiveness of this dietary component in stimulating growth and development. This geese diet contributed not only to the improvement of poultry meat yield, but also to an increase in its protein content by 5.0 %, confirming the improvement in the quality characteristics of the product.

A positive influence of oats and alfalfa on the technological characteristics of meat during low-temperature storage was established, namely, an increase in the ability of meat to retain moisture and a smaller loss of mass during defrosting. There was also an increase in the content of ω3-polyunsaturated fatty acids, vitamin E, β-carotene, as well as the essential amino acids threonine and methionine, while the level of other essential amino acids remained at the level of the meat of the control group.

During low-temperature storage in the meat of this experimental group, the processes of peroxide oxidation were activated 12 days later than in the corresponding samples of the control group. At the end of storage, a significantly higher content of vitamin E, β-carotene and ω3-PUFA was found in the meat of the experimental group. The content of essential amino acids valine, leucine and isoleucine in the experimental sample also exceeded the corresponding indicators of the control group. However, the meat of the experimental group was characterized by a lower content

of phenylalanine. Thus, the admixture of oats and alfalfa in the geese diet contributes to the enrichment of meat with important food components. These positive changes are preserved even during long-term low-temperature storage, which ensures an increase in the nutritional value of meat products.

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Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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CHAPTER 9

Justification of the technology for the use of Phyllophora (Zernov field) carrageenan as a regulator of the consistency of food products

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Abstract

The results of theoretical and experimental studies and progressive solutions regarding the use of the phytocolloid – carrageenan Phyllophora (Zernov field) extracted from the Black Sea red algae Phyllophora Brodyas food consistency regulator is presented. The technological aspects of the use of carrageenan from the Black Sea red algae Phyllophora Brody are substantiated. The study shows that the use of this drug ("PZF" carrageenan) is appropriate for expanding the range of consistency regulators of food industry products. It is found that "PZF" carrageenan extracted from the Black Sea red algae Phyllophora Brody has a 3.6-anhydrogalactose content of 21.3 %; the mass fraction of sulfoether groups (in terms of SO_4) is 24.2 %. The concentration dependence of the viscosity of the carrageenan solutions "PZF" is studied. With an increase in the concentration of "PZF" carrageenan to 2 %, the flow index of the solution decreases sharply, which indicates an increase in the structuredness of the system. The dependence of the viscosity of the "PZF" carrageenan solutions on the shear rate gradient in the interval 3–1312 s^{-1} is established. In the studied range of shear rates, the viscosity of solutions obeys the power law and is described by the Ostwald-Weyl equation. It is found that the reversible destruction of the structure occurs under the action of shear. The degree of thixotropic reduction of the "PZF" carrageenan solution is 87.9 %. The influence of temperature and pH on the rheological properties of "PZF" carrageenan solutions is studied. It is found that at temperatures up to 45 °C, carrageenan macromolecules exist in a spiral conformation, and at higher temperatures they undergo a thermoreversible transition into a coil conformation. This transition causes a decrease in viscosity and gelation of the solution. It is found that "PZF" carrageenan solutions retain their abnormally viscous properties in a wide pH range. When the pH of the

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solution changes from 1 to 11, no signs of a conformational transition of macromolecules of "PZF" carrageenan are detected. In the process of storage, the viscosity of "PZF" carrageenan solutions first increased, and then decreased, regardless of the pH value. A solution with pH=4 has high stability during storage. An acidic environment prevents the development of microorganisms; however, in this case it is not strong enough to cause significant hydrolysis of the polysaccharide. The obtained data on the chemical and physic-mechanical properties of "PZF" carrageenan solutions make it possible to predict the properties of viscous solutions and gels for structured food products.

Keywords

Carrageenan, phytocolloid, consistency regulator, extraction, rheological properties, physical and chemical properties, food technology.

9.1 Justification of using carrageenan feasibility as regulators of food products consistency

9.1.1 Analysis of modern theoretical information on the gel-forming ability of carrageenan

Carrageenan is an anionic sulfated polysaccharide consisting of alternating long linear chains of (1→3)-β-d-galactose and (1→4)-3.6-anhydro-α-d-galactose (3.6-AG) or (1→4)-α-d-galactose with ether sulfates (15–40 %) [1]. These natural polymers are divided into six main forms based on their source, solubility, and sulfate content: kappa, iota, lambda, mu, nu, and theta. Thanks to the numerous works of Riess and co-authors [2], several "saturated", i.e., idealized structures of carrageenan were established. This made it possible to divide carrageenans into so-called "types", which differ in the content of 3.6-anhydro-galactose, the location and number of sulfate groups. Currently, more than 16 carrageenan structures are known, but the main ones are the so-called gelling types, which include kappa- and iota-carrageenans, and non-gelling lambda-carrageenans. These types of carrageenans are of commercial value [3–5].

The practical use of carrageenan is largely determined by its physicochemical properties, which are dissimilar for different types of carrageenans. The gelling properties of carrageenans depend on their chemical structure, the nature of the cation, the temperature of the solution, and the concentration of the polymer. The gelling properties are higher, the fewer the residues of sulfuric acid in the polysaccharide and the higher the content of 3.6-dihydrogalactose in it. Increasing the content

of the latter from 28 to 35 % leads to a significant increase in gelling properties, which can be achieved by special alkaline treatment [6]. Due to the presence of a highly charged sulfate group in the polymer molecule, carrageenans are in solution in the form of stable K^+, Na^+ or Ca^{++} salts. The nature of the cation determines the gelling properties of the polysaccharide. Natural extracts have various gelling properties. Kappa carrageenan does not gel in the Na^+ form, but the addition of K^+, Ca^{++} or NH_4 in the case of kappa and Ca^{++} in the case of iota promotes the formation of stable transparent gels.

The viscosity of aqueous solutions of carrageenans depends on their type, temperature and pH of the solution, the presence or absence of ions, the concentration and molecular weight of the polymer. Similar to other polysaccharides that have a charge along the entire chain of the macromolecule, the viscosity of solutions increases with increasing concentration and molecular weight of carrageenan and decreases with increasing temperature and ionic strength of the solution. Most commercial samples of carrageenan form solutions with a viscosity of 25 to 500 mPa and a core area of 25 to 100 mPa. At the same time, native lambda-carrageenan can produce solutions with a viscosity of up to 20,000 mPa [5].

Kappa, iota and lambda carrageenans are rationally used as food consistency regulators due to their viscoelastic and gelling properties.

Fig. 9.1 shows the chemical structures of gelling carrageenans, which are the most commercially used. Iota-carrageenan (Iota) is a nearly homopolymer of G4S-DA2S disaccharide units, containing a very low amount (about 5 mol %) of G4S-DA disaccharide units. Kappa-carrageenan (Kappa) is slightly more heterogeneous, up to 10 mol % of G4S-DA2S disaccharide units break blocks of G4S-DA disaccharide units [6]. A third gelling carrageenan, commercially known as kappa-2 or weak kappa (Kappa 2), has gradually received an industrial boost. Kappa 2 replaces Kappa and Iota blends in niche applications where intermediate gelling properties are required between the hard and brittle gels formed by Kappa and the softer but deformable gels formed by Iota [1]. Kappa 2 is a random block copolymer made of G4S-DA sequences (representing 45–80 mol % of the hybrid chain) [7, 8] and G4S-DA2S [9, 10]. Depending on the seaweed and the extraction method used for isolation polysaccharide, the G4S-DA and G4S-DA2S blocks can be separated by more sulfitated disaccharide units, such as G4S-D6S (mu-carrageenan) and G4S-D2S,6S (nu-carrageenan) [11].

In his comprehensive review of the gelation of carrageenans, Piculell gathered compelling evidence for network formation at the superhelical level for kappa gels, giving hard gels in contrast to soft Iota gels, where the network can occur in a helix. Fewer studies have attempted to systematically compare the network

structure of carrageenan with the corresponding elastic properties of the gel in order to identify structure-elasticity relationships. The purpose of the article [5] is to review the recent progress made in defining such relationships. The aim is to show the lack of rationalization of structural and elastic data by theories developed to describe the special elasticity of filamentous networks. The latter have been used with some success to elucidate the relationship between structure and rheological properties in various biopolymers and polymer gels that have structural and elastic similarities to carrageenan gels. L. Hilliou showed that reports on nonlinear rheological properties of carrageenan gels are still critically lacking in the literature, as emphasized by Van de Velde [8]. The significance of nonlinear elastic properties for the identification of structural features in these networks is emphasized. Preliminary nonlinear rheological data for Kappa, Iota, and Kappa 2 gels are presented. These results demonstrate concentration scaling in the strain-hardening behavior of Iota and Kappa 2 gels. The strain-hardening is analyzed using theories to extract elastically relevant structural features for comparison with structural information.

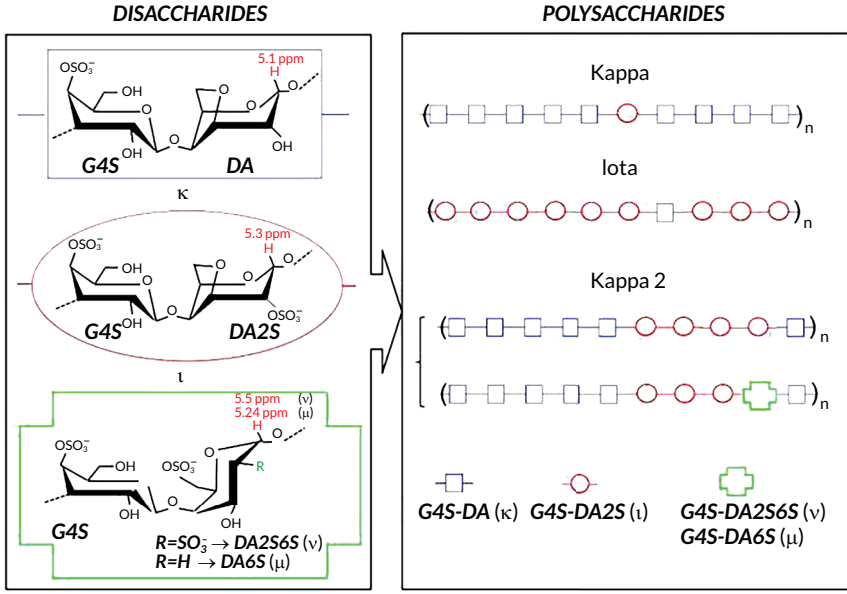

Fig. 9.1 Chemical structures of industrially suitable gel-forming carrageenans

Although many studies used commercial samples as received, most of the results presented here were obtained after performing a purification step to obtain a polyelectrolyte with one type of counterion. This is of primary importance for Kappa, which is known to exhibit specific gel properties depending on the type of salt used to form the gels [12]. In contrast, it was found that Iota does not show such sensitivity to cations unless a significant amount of G4S-DA units remain present as impurities in Iota [13].

Overall, the picture that emerges from the data reviewed by L. Hilliou is that the large differences in the elasticity of the Iota and Kappa gels are difficult to reconcile with their rather similar structures, which essentially consist of semi-flexible filaments with a length *L* of the order of 100 nm and a thickness *d* of the order of 10 nm, located in a dense network with cell size ε of the order of nanometers or tens of nanometers. Structural heterogeneity, where different filament types coexist with different filament aggregates, has long been reported in carrageenan gels. Structural heterogeneity on length scales larger than 100 nm and with correlations in the micron was recently revealed by confocal scanning laser microscopy in Kappa gels, showing significant turbidity in contrast to the uniform and clear Iota gels.

The reviewed here literature on the relationship between gel structure and elastic properties provides ample evidence for the filamentous nature of responsible for the elasticity of carrageenan gels networks. This structure explains the power-law dependence of the linear modulus of elasticity of the gel on the concentration of carrageenan and the strain hardening behavior of Iota gels. Although it is not well documented in the literature, strain failure has been established in a study [14] and rationalized by theoretical models. The latter explains the quadratic concentration scaling of strain hardening, which arises from the rod-like shape of the filaments (with fractal dimensions of 1.7 rank), which gives the network more enthalpic elasticity than entropy. The picture for kappa-gels is much less clear, since difficulties in rheological testing of these materials may explain the scatter of power-law values reported in the reviewed literature to describe the concentration dependence of G0. Due to its longer persistence, Kappa self-assembles into straighter and more connected strands compared to Iota. However, a review of the literature shows that both systems exhibit nearly identical chain lengths (about 100 nm) and radii (about 1 nm). It is also reported that the cell sizes in the network are almost the same. Thus, the higher elasticity of kappa gels is attributed to the greater stiffness of the kappa filaments (or filaments), as suggested by the authors who found that kappa forms straighter filaments [15]. Several recent theoretical developments in the elasticity of filamentous networks, briefly

reviewed here, suggest that kappa-gels should exhibit strain hardening in this case. However, strain rarefaction followed by abrupt gel failure is consistently reported in the limited sample of literature reviewed here. This study confirms this high deformation behavior. Based on the results of the literature review, it can be concluded that reoptic measurements will help determine structural changes in the behavior of large deformations. Nonlinear elasticity should be studied using additional methods that include strain time [16], without limiting the study to dynamic vibration tests. In particular, such time must be taken into account when studying the thixotropy of carrageenan gels, which is a matter of industrial interest. Thus, the specific extraction of carrageenans from selected seaweeds seems preferable to the conversion of commercial samples into a single cationic form, since such processes are known to degrade the polysaccharide [17]. It is expedient to study the physicochemical properties of carrageenan extracted from red seaweed, which can be obtained in industrial quantities from undeveloped natural sources.

9.1.2 Use of carrageenan in the food industry

Natural food additives, which are able to adjust the beneficial properties and chemical composition of food products, are of particular value for the creation of full-fledged food products for mass and medical and preventive purposes. In the developed countries of the world, there is a constant increase in the production of carrageenan. In the early 1990s, its annual production reached 15.5 thousand tons, and now it is 30 thousand tons [18]. The main companies that produce carrageenan are concentrated in Europe and the USA, its production is developing very actively in the Philippines, Chile and China. The annual sale of carrageenan in the world is more than 200 million USD. The increase in the production of this polysaccharide-hydrocolloid is due to the increase in demand for food products containing carrageenan.

Currently, the food industry uses 80 % of all manufactured carrageenan, and the average consumption of this product is 250 mg/day per person [4]. The use of carrageenan in food products is based on the general recognition of its "safeness". In the USA and EU countries, carrageenan is considered safe and useful, approved for use as a food additive. In Japan, it is considered a "natural product" and is not subject to the rules governing the use of food additives.

Leading international health organizations such as the World Health Organization (WHO), the US Food and Drug Administration, the European Union, Health

Canada and other independent international organizations allow the use of carrageenan in food products because it is absolutely safe for human consumption. This is confirmed by comprehensive research by scientists conducted in July 2014 – Carrageenan in Infant Formula [19, 20].

After a comprehensive scientific review of carrageenans by scientists in July 2014, the World Health Organization (WHO) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) concluded that carrageenan is safe for use in formula milk, including infant formula children with special diseases. Moreover, carrageenan is an important component of such infant formulas, as it is a source of essential nutrients available to the child's body.

Currently, more than 150 different carrageenan-containing products are produced in the world. The main branches of the food industry that use carrageenan are dairy, confectionery and meat.

Different fractions of carrageenan are widely used in the food industry for gelation, thickening and stabilization of emulsions in systems, on milk and water. They are often used to balance and improve the properties of other gels, as they have the ability to form complexes with other hydrocolloids.

Carrageenan is superior to agar and alginate in cases where high viscosity and accompanying thickening, emulsification and suspension are required. Thus, at low concentrations (0.01–0.03 %), it suspends cocoa particles and prevents the separation of fats during the preparation of pasteurized chocolate milk, soy protein drinks with chocolate additives. Kappa-carrageenan within a narrow range of viscosity, from 7 to 10 mPa, exhibits special properties – it prevents the ability to thicken milk, even at high concentrations, so it can be used as an additive to milk and ice cream. It stabilizes fat in ice cream, condensed milk, baby formula, vegetable oil for salads.

Lambda-carrageenan does not gel by itself, but provides thickening and stabilization of cold milk and is used for the preparation of cold chocolate milk, for thickening and stabilization of quick-dissolving powdered milk puddings, fruit drinks, as well as drinks based on natural plant raw materials, syrups, cheese spreads. Dairy products containing carrageenan do not require homogenization during preparation, the presence of lambda-carrageenan in them gives them a mousse structure.

The quality and range of confectionery products are largely determined by the availability and quality of the used gelling agents – emulsifiers and stabilizers. Carrageenans have a relatively high melting point, and this property is used for the preparation at room temperature of specific fruit confections, very plastic milk puddings of the "zhuangdong – soft ice" type. The aqueous gelling characteristics

of carrageenan are particularly useful in diet foods such as jellies and low-sugar syrups [5].

In the production of creamy desserts, carrageenan significantly affects the rheological properties of the final product. Each manufacturer can choose the appropriate concentration of carrageenan for their technological system in order to produce a product that appeals to the consumer, with maximum shelf life and resistance to the processes of retrogradation and syneresis.

Modified carrageenans have an obvious protective property against fat oxidation and therefore can be used as ideal antioxidants. In the form of a coagulate, carrageenan can be used as a fixative in canned meat, fruit gels, and jellies. Moreover, the polysaccharide added to the mixture with water, to the defatted minced meat, gives the meat its original taste. At the end of 1990, the McDonald's company began trial marketing of low-fat hamburgers called LeenDelux, the fat content of which was reduced by 91 %. Carrageenan gives cutlets juiciness and keeps their shape. At the same time, the taste of the cutlets does not deteriorate.

Specific examples of the use of carrageenan in food products testify to the excessive variety of areas of use of this polysaccharide.

The amount of carrageenan in food products usually does not exceed 2 % and in this concentration it cannot affect digestion. If this amount is exceeded, the process of assimilation of food slows down and there is a feeling of satiety, which in no way affects the further absorption of food in the intestines, so it is possible to hope that carrageenan will be used to prepare products that "increase the feeling of satiety".

Equally important is the fact that carrageenan has a wide range of different biological activities. Pharmacological studies have shown that it has immunostimulating and immunosuppressive effects; it has anticoagulant activity (primarily antithrombotic effect); is an enterosorbent and can be used to remove heavy metals from the body; inhibits lung metastases; used to treat atopic ulcers. Thus, carrageenan is a unique basis for the creation of new therapeutic and preventive products and drugs. Carrageenan is certified for use in EU countries. It is in such products that the food industry "feels" an acute shortage.

9.2 Research materials and methods

9.2.1 Block diagram of research

Theoretical and experimental studies were carried out according to the block diagram shown in **Fig. 9.2**.

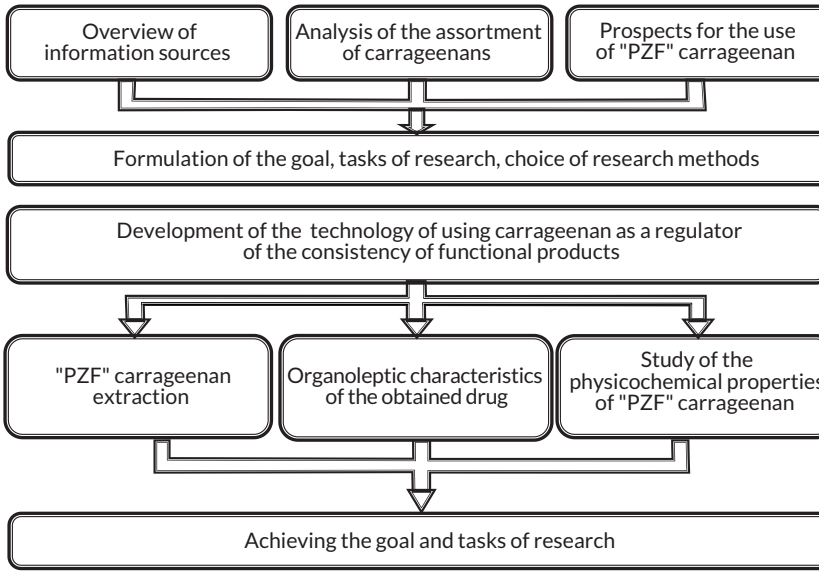

Fig. 9.2 Block diagram of conducting theoretical and experimental research

9.2.2 Object of study

Characteristics of "PZF" carrageenan: moisture – 11 %, mass fraction of ash – 25.5 %. The content of 3.6-anhydrogalactose is 21.3 %, the mass fraction of sulfoester groups (in terms of SO_4) is 24.2 %.

9.2.3 Materials, reagents and equipment

9.2.3.1 Products and reagents

Product: Acetic acid. Acetic acid is an organic compound, a monobasic carboxylic acid of the composition CH_3COOH. It is produced in accordance with the national standard DSTU 2450:2006 "Vinegars from food raw materials. General technical conditions". Food supplement E260.

Product: Baking soda. Chemical name: sodium bicarbonate. Chemical formula: $NaHCO_3$. Baking soda is a crystalline powder-like substance of fine grinding, white

in color, odorless. A distinctive feature of baking soda is its mild alkaline properties, which do not have a negative effect on plant and animal tissues. GOST 2156. Food supplement E500.

Product: Technical resorcinol. Chemical name: resorcinol. Chemical formula: $C_6H_6O_2$. White, slightly yellowish scales with a specific smell. Water-soluble, soluble in alcohol, diethyl ether. Hardly soluble in benzene, carbon disulfide, chloroform. The chemical properties are the same as those of phenols. Resorcinol requires careful handling, as its vapors and dust are irritating to the respiratory tract and eyes. CAS: 108-46-3.

Product: Rectified ethyl alcohol. Chemical name: ethanol. Chemical formula: C_2H_5OH. Colorless liquid product, clear characteristic odor and fiery taste obtained by distillation of the must from the alcoholic fermentation of the molasses, subsequently rectified. The alcoholic strength achieved during distillation must not be less than 96 % Vol. DSTU 4221:2003.

Product: Granulated sugar. Chemical name: Sucrose. Chemical formula: $C_{12}H_{22}O_{11}$. It is sucrose in the form of separate white or white with yellowish crystals with sizes ranging from 0.2 to 2.5 mm. The mass fraction of sucrose is 99.55–99.75 % (in terms of dry matter). Mass fraction of moisture – 0.14–0.15 %. In addition to direct use by the population as food, granulated sugar is widely used in the food industry for the production of canned milk, baby food, in the biopharmaceutical industry, etc. DSTU 2316.

Product: Potassium hydroxide. Chemical name: Potassium hydroxide. Chemical formula: KOH. Colorless, very hygroscopic crystals, but less hygroscopic than sodium hydroxide. Aqueous solutions of KOH are highly alkaline. It has many industrial and niche applications, most of which utilize its caustic nature and its reactivity toward acids. TU 20.13.25-025-5227004-2015.

Product: Potassium chloride. Chemical name: Potassium chloride. Chemical formula: KCl. Potassium chloride is a metal halide salt composed of potassium and chlorine. It is odorless and has a white or colorless vitreous crystal appearance. The solid dissolves readily in water, and its solutions have a salt-like taste. TU 2184-042-00209527-97.

Product: Hydrochloric acid. Chemical name: Hydrochloric acid. Chemical formula: HCl. Hydrochloric acid is the aqueous solution of hydrogen chloride gas and the main component of gastric acid, an acid produced naturally in the human stomach to help digest food. Hydrochloric acid is produced synthetically for a variety of industrial and commercial applications. DSTU 3118.

Product: Isopropyl alcohol. Chemical name: Isopropyl alcohol. Chemical formula: C_3H_8O. Colorless transparent liquid with a bitter taste and a sharp smell of alcohol

and acetone. Isopropanol is used as a disinfectant to kill bacteria, viruses and fungi, as well as to clean surfaces and treat skin before injections. Contained in household cleaners and hand sanitizers. DSTU 9805:84.

Product: Phenolphthalein. Chemical name: Phenolphthalein. Chemical formula: $C_{20}H_{14}O_4$. Triphenylmethane dye, an acid-base indicator that changes color from colorless to red-violet, "crimson". At pH>12 the indicator becomes discolored again. TU 6-09-5360-88.

Equipment and chemical utensils:

– Rheotest-2 rotary viscometer (Germany) (**Fig. 9.3**);
– pH meter pH-121 (**Fig. 9.4**);
– KFK-2MP photoelectrocolorimeter (**Fig. 9.5**);
– technical scales;
– laboratory ionometer;
– electric plates;
– chopper of vegetable raw materials;
– containers;
– precision refractometer;
– water bath;
– stopwatch;
– viscometers;
– measuring flasks, conical flasks, chemical glasses, graduated pipettes;
– burettes, watering cans;
– tripods with rings;
– filter paper.

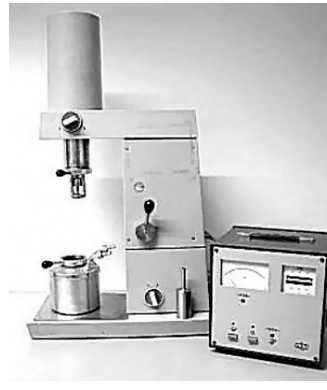

Fig. 9.3 Rheotest-2 rotary viscometer (Germany)

Fig. 9.4 pH meter pH-121

Fig. 9.5 KFK-2MP photoelectrocolorimeter

9.2.4 Research methods

9.2.4.1 Determination of the content of 3.6-anhydrogalactose in "PZF" carrageenan according to the modified Yafe method

2 ml of the test solution (sample) was added to one test tube with a polished reflux condenser, and 2 ml of the standard solution (control) to the second. Then 2 ml of a 0.1 % solution of resorcinol in 96 % ethyl alcohol and 6 ml of a 30 % solution of hydrochloric acid were added to both test tubes. The contents of the test tubes were mixed and heated in a water bath for 8 min at a temperature of 80. After heating, the solutions were cooled and colorimetric at a wavelength of 490 nm [21].

The extinction value of the solution containing the condensation product of oxymethylfurfural formed from 3.6-anhydrogalactose with resorcinol was determined.

The mass concentration of 3.6-anhydrogalactose in the test sample (μg/ml) was calculated according to the formula:

$$C = \frac{Q \cdot E_1}{E_0},$$

where E_1 and E_0 – extinction of the tested and standard solutions, respectively; Q – coefficient that is the ratio of the mass concentration in the standard sample to the volume of the sample.

9.2.4.2 Determination of the content of sulfoester groups in "PZF" carrageenan

Determination of the content of sulfoester groups in "PZF" carrageenan was carried out gravimetrically in the form of $BaSO_4$.

9.2.4.3 Assessment of organoleptic characteristics

The main requirements for carrageenans are listed in **Table 9.1**.

Table 9.1 Requirements for the release form of carrageenan

Name of the indicator	Characteristic and norm
Appearance	Finely dispersed powder
Color	From light cream to beige
The smell of carrageenan and gel with a mass fraction of dry carrageenan 0.85 %	Neutral
The taste of the gel with a mass fraction of dry carrageenan 0.85 %	No extraneous aftertaste
The presence of extraneous impurities	Is not allowed

9.2.4.4 Determination of carrageenan solubility

Refractive indices were measured on an IRF-23 refractometer at a temperature of 25 °C. 1 g of the drug was added to 100 g of water and the resulting mixture was

heated in a water bath at a rate of 0.5 °C/min. Every 10 minutes, the value of the refractive index of the mixture was determined. The dissolution was considered complete if the value of the refractive index of the composition acquired a constant value.

9.2.4.5 Study of rheological characteristics

The rotary viscometer Rheotest-2 (Germany) was used to determine the viscosity of Newtonian liquids and conduct rheological studies of non-Newtonian systems [21]. Measuring node – coaxial cylinders.

The range of changing shear rate gradient is from 3 to 1312 s^{-1}.

The temperature of the measuring unit was kept with an accuracy of 0.1 °C.

The dependence of viscosity on the shear rate was calculated using the computer program "Techiya".

9.2.4.6 Determination of thixotropic reduction degree of the solutions viscosity

The value of the degree of thixotropic reduction of viscosity of "PZF" carrageenan solutions was calculated by the formula:

$$S = \frac{1}{n}\sum_{i}^{n}\frac{\eta_{1i}}{\eta_{0i}}\cdot 100\ \%,$$

where S – the degree of thixotropic restoration of viscosity, %; n – the number of fixed values of the shear rate gradient; η_{0i} – the viscosity at the i-th shear rate, which is measured in the mode increasing shear rate gradient, Pa·s; η_{1i} – the viscosity at the i-th shear rate, which is measured in the mode descending gradient and shear rate, Pa·s.

9.2.4.7 Determination of the pH indicator

One of the main physico-chemical indicators determining the course of the technological process is pH. Hydrogen indicator pH is a value that shows the degree of activity of hydrogen ions (H+) in a solution, that is, the degree of acidity or alkalinity of this solution. This characteristic determines the structure formation in the finished product, as well as its storage terms.

The pH of the solutions was determined according to the standard procedure.

To determine the pH, 100 g of a 1 % suspension of the carrageenan preparation in distilled water was prepared. The suspension is dispersed for 15 min at room temperature and the pH is determined on a pH meter pre-calibrated with standard buffers.

9.3 Research results and discussion

9.3.1 Determination of the "PZF" carrageenan characteristics, which determine the possibility of its use as a regulator of food products consistency

9.3.1.1 Determination of the 3.6-anhydrogalactose content in "PZF" carrageenan

Carrageenans (sulfated red seaweed galactans) are a unique class of polysaccharides. The basis of the molecules of most galactans is a carbohydrate chain built from alternating residues of (1→3)-β-d-galactopyranose and (1→4)-α-galactopyranose. These 4-linked residues can be partially or completely in the form of a 3.6-anhydro derivative and belong to the D-series.

It is known that a necessary condition for the manifestation of gelling properties is a high content of 3.6-anhydrogalactose residues and a high level of regularity of the structure of polysaccharides.

Compared to other natural polysaccharides, the use of chemical methods in galactans from red algae has a number of features associated with the presence of 3.6-anhydrogalactose and sulfate groups.

An important component of galactans, 3.6-anhydrogalactose is the only 3.6-anhydrohexose found in nature, and it is not found anywhere except in red algae. This monosaccharide is highly prone to degradation in an acidic environment, so that under the conditions of acid hydrolysis of glycosidic bonds, which is used to determine the monosaccharide composition of polysaccharides, 3.6 anhydrogalactose is completely destroyed. Such easy destruction allows selective determination of 3.6-anhydrogalactose in the presence of other sugars by color reaction with resorcinol.

In this research, the determination of the content of 3.6-anhydrogalactose in the studied "PZF" carrageenan was carried out according to the colorimetric resorcinol method of Jaffe (color reaction with resorcinol) with a minor modification proposed by the researchers [21]. The resorcinol reagent was prepared 3 hours before the colorimetric study. Briefly, resorcinol reagent was prepared from 9 ml of resorcinol

solution (1.5 mg/ml), 1 ml of acetaldehyde solution (0.04 vol/vol %) and 100 ml of concentrated hydrochloric acid. Next, a 0.03 ml aliquot of the sample solution (1 mg/ml) was added to a centrifuge tube followed by the addition of 0.2 ml of distilled water. After placing in an ice bath for 5 minutes, 1 ml of resorcinol reagent was added, homogeneously mixed in an ice bath, and then placed at room temperature for 2 minutes. The mixture was incubated for 10 minutes at 80 °C, followed by cooling for 5 minutes in an ice bath. The absorbance of 3.6-anhydrogalactose was measured at 555 nm, and the concentration of 3.6-anhydrogalactose was calculated using a calibration curve with galactose standards. All samples were analyzed in triplicate.

According to the research results, the content of 3.6-anhydrogalactose in "PZF" carrageenan is 21.3 %. This is a high content of this component in the general structure of carrageenan. A high content of this monomer can affect the physical and chemical properties of carrageenan. The high content of 3.6-anhydrogalactose in "PZF" carrageenan characterizes it as a drug potentially prone to gel formation and gives grounds for its potential use in functional food products.

9.3.2 Study of rheological properties of "PZF" carrageenan

Much attention is paid to the rheological properties of food products, because they determine the quality of condensed or emulsion products and their storage stability [22–24].

When performing the work, a study of the rheological properties of "PZF" carrageenan gels of various concentrations was carried out.

Systems with a concentration of 0.07 %; 0.08 %; 0.1 %; 0.15 %; 0.2 %; 0.3 %; 0.4 %; 0.5 %; 0.6 %; 0.7 %; 0.8 %; 0.9 %; 1 %; 1.5 %; 2 % were studied.

There are several approaches to the graphical interpretation of the concentration dependence of the viscosity of polymer solutions. The relationship between the viscosity of solutions of almost any polysaccharide and its concentration is exponential.

The dependence of the viscosity of "PZF" carrageenan solutions on the shear rate gradient in the interval 3–1312 s^{-1} was established. As for most high-molecular systems, with an increase in the shear rate, there is an anomalous decrease in viscosity. The obtained dependences are, most likely, sections of the "structural branches" of the complete rheological curves, since there are no signs of a transition to the regimes of flow with the highest or lowest viscosity.

In the studied range of shear rates, the viscosity of solutions obeys the power law and is described by the Ostwald-Weyl equation:

$$\eta = \frac{P}{\dot{\gamma}} = k\dot{\gamma}^{n-1}.$$

The values of the constants *k* and *n* of the equation for 0.1–2 % of "PZF" carrageenan solutions are given in the **Table 9.2**.

Table 9.2 The value of the Ostwald-Weyl equation constants

Carrageenan concentration "PZF", %	*k*, Pa·s	*n*
0.1	$3.7 \cdot 10^{-3}$	0.950
0.3	0.234	0.609
0.5	5.320	0.420
1.0	7.467	0.411
2.0	10.43	0.403

With an increase in the concentration of "PZF" carrageenan to 2 %, the flow index of the solution decreases sharply, which indicates an increase in the structure of the system. Solutions containing more than 2 % "PZF" carrageenan have a fairly developed spatial structure.

Marmalade, jelly candies, fruit jelly desserts have a jelly-like structure. Their technology involves boiling the recipe mixture, processing the marmalade mass, forming, drying. During these technological stages, the mass transitions from the sol state to the gel state. The structure of the gel is characteristic of the finished product. In production, there are situations when the mass prepared for forming, due to various reasons, cannot be formed. Then the transition of the sol structure to the gel structure occurs. There is a need for the reverse process – converting the gel into a sol. In this context, the application of thixotropic properties is important [25].

The process of thixotropic restoration of the viscosity of "PZF" carrageenan solutions, which is represented by the "direct" and "reverse" branches of the viscosity dependence on the shear rate, was studied.

According to the results of experimental data, the degree of thixotropic restoration of viscosity of 1 % "PZF" carrageenan solutions is:

$$S = 87.9\ \%.$$

When studying thixotropies of gels containing carrageenan, the authors [23] noted that thixotropic recovery is never complete. For cold shear of already formed gels, ripening time before shear was not a significant factor for aqueous gels, but caused

significant differences in the final texture of the model desserts. In our studies of the "PZF" carrageenan solution, the presence of hysteresis was revealed when measuring the effective viscosity in the modes of increasing and decreasing shear rate gradient. This indicates that reversible changes associated with the internal structure occur during the shear impact, but additional research is still required to establish the nature of the structural changes occurring.

9.3.2.1 Determination of the content of sulfoester groups

In addition to 3.6-anhydrogalactose, sulfate groups are an equally important structural element of galactans that determines their properties and chemical behavior. These groups are cleaved in an acidic environment at rates comparable to the rate of hydrolysis of galactoside bonds, so that complete acid hydrolysis of the polysaccharide also results in complete desulfation. In an alkaline environment, including polysaccharide methylation conditions, sulfate groups are usually stable, with one exception: the sulfate at position 6 of the galactose residue bound at position 4 easily undergoes intramolecular substitution with a free hydroxyl at C-3 to form 3.6-anhydrogalactose.

This sequence of reactions (enzymatic sulfation of C-6 followed by enzymatic elimination of sulfuric acid, which leads to the formation of a 3.6-anhydrocycle) is the basis of the biosynthesis of 3.6-anhydrogalactose residues in the galactans of red algae, and in industry, alkaline treatment of algae is often used to increase the content of 3.6-anhydrogalactose and, therefore, to improve the gel-forming properties of polysaccharides released.

Determination of the content of sulfoester groups in "PZF" carrageenan was carried out by the gravimetric method in the form of $BaSO_4$.

The method is based on the precipitation of sulfate ions in the form of a crystalline white precipitate of $BaSO_4$ and obtaining the gravimetric form ($BaSO_4$) by calcinations:

$$SO_4^{2-} + Ba^{2+} = BaSO_4.$$

During research, the attention was paid to the process of obtaining the precipitated form. As soon as the sediment settles and the liquid above it becomes clear, check the completeness of the $BaSO_4$ precipitation. To do this, 2–3 drops of hot solution of $BaCl_2$ are added to the solution above the sediment, being careful not to disturb the sediment. If no turbidity of the solution is observed, the completeness of the precipitation is achieved, otherwise add another 1 ml of hot solution of $BaCl_2$, allow the precipitate to settle and check the completeness of the precipitation again.

Then the beaker is placed, heated for 2–3 hours to ripen the sediment, after which the sediment is filtered and washed.

To check the completeness of sediment washing, a few drops of filtrate are taken on a watch glass and a qualitative reaction is carried out for chloride ions, from which the sediment is washed. Rinsing ends with a negative test result.

After the end of ashing, the sediment in the crucible is roasted in a muffle furnace at a temperature of 800 °C until a constant mass of the crucible with a gravimetric form is obtained.

Based on the results of the analysis, calculate the mass of sulfate (SO_4) in the sample. The proportion is:

1 mol of $BaSO_4$ (233.4 g) contains 1 mol of SO_4 (96.06 g);
in *m* g – *x* g.

According to the experiment, the weight of the ashed sediment is 0.588 g.

Thus, the mass fraction of sulfoester groups in "PZF" carrageenan (in terms of SO_4) is 24.2 %.

In accordance with international legislation, carrageenans, as commercial preparations for the food industry, must have a sulfoester group content of at least 20 %. That is, the studied "PZF" carrageenan according to the characteristic – the content of sulfoester groups meets the requirements for commercial carrageenans for the food industry.

When discussing the obtained results, it should be noted that κ-carrageenan consists of a repeating unit consisting of a disaccharide, β-(1→3)-d-galactose-4-sulfate and α-(1→4)-3.6-anhydro-d-galactose. ι-carrageenan has two sulfate groups in the disaccharide repeating unit; β-(1→3)-d-galactose-4-sulfate and α-(1→4)-3.6-anhydro-d-galactose-2-sulfate. λ-carrageenan consists of β-(1-3)-d-galactose-2-sulfate and α-(1→4)-d-galactose-2,6-disulfate, including three sulfate groups. It should be noted that the presented structure is ideal, and real samples contain a number of different types of sequences. Under appropriate conditions, κ-carrageenan and ι-carrageenan in aqueous solutions undergo a thermoreversible sol-gel transition, while gelation does not occur in λ-carrageenan with a larger number of electrolyte groups. It is widely recognized that the gelation of carrageenan is based on the formation of a double helical structure. Carrageenan adopts a random helix conformation in the sol state, and low temperature induces the anhydro-galactose sequences to twist in a double helical fashion. Further aggregation also favors the formed double helical moieties. Part of the hydrate sequences functions as a helix break. Eventually, the aggregation of the double helices forms a domain of crosslinks and leads to

an infinite network structure sufficient to complete gelation. Since the repeating units of carrageenan have an electric charge in the sulfate groups, counterions have been found to play a role in gelation.

Thus, the experimentally determined mass fraction of sulfoester groups in "PZF" carrageenan (in terms of SO_4), which is 24.2 %, gives reason to consider "PZF" carrageenan potentially suitable for gelation. Therefore, it is advisable to carry out further research in the direction of studying the rheological properties of the viscous systems that it forms, in conditions that are realistically close to the technologies for making jelly desserts.

9.3.3 Study of the temperature influence on the rheological properties of "PZF" carrageenan solutions

In practice, solutions of polysaccharides, which are used to adjust the consistency of food products, are subjected to temperature effects. This determines the theoretical and practical interest of data characterizing the effect of temperature on the rheological properties of "PZF" carrageenan solutions.

Fig. 9.6 shows the dependence of the viscosity of the "PZF" carrageenan solution on temperature.

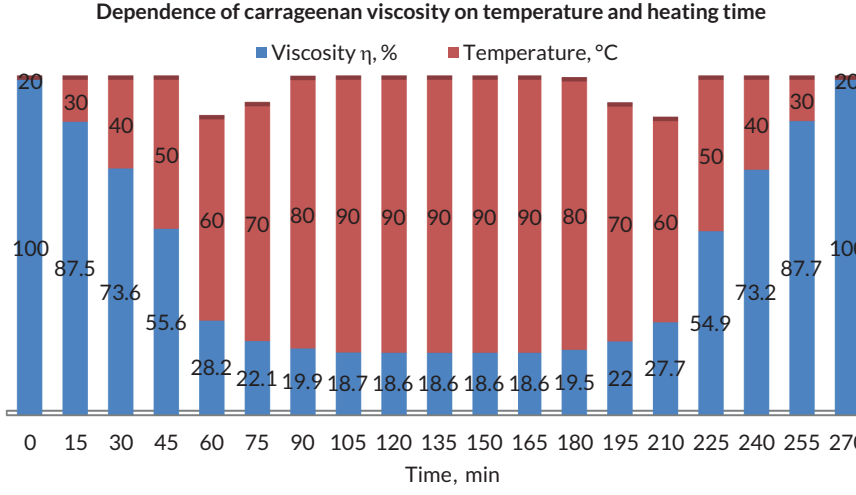

Fig. 9.6 Diagram of the dependence of carrageenan solution viscosity on temperature and heating time

As the temperature rises from 25 °C to 40–45 °C, a relatively small decrease in viscosity is observed. A further increase in temperature above 45 °C leads to a sharp drop in viscosity, at 70–90 °C the decrease in viscosity becomes pronounced. The resulting dependence is practically symmetrical with respect to the inflection point. A somewhat unusual temperature dependence of the viscosity of the "PZF" carrageenan solution was revealed. It can be assumed that the most probable cause is a change in the conformation of the "PZF" carrageenan macromolecules under the influence of temperature. This assumption is due to the fact that in concentrated solutions at normal temperatures, sulfated galactans (including carrageenans) are in a spiral conformation. On the other hand, an increase in the intensity of thermal motion in such solutions inevitably leads to the transition of a high-molecular compound from one conformation to another, and, in the absence of chemical transformations, from a more ordered to a less ordered one.

As a rule, low temperatures and even freezing are used to preserve food products. The thermal stability of food products under conditions of freezing and thawing is a very important factor that determines the quality of the product during storage, so the next stage was to investigate the effect of low temperatures on the rheological and thixotropic properties of carrageenan gels.

Before the experiment, gels from "PZF" carrageenan were pre-frozen at a temperature of –18 °C and after thawing were subjected to research.

It was established that after thawing, the gels formed by "PZF" carrageenan lose their strength the more the concentration of carrageenan is higher. Thus, gels with concentrations of 3 g/l lost 29 %, 5 g/l – 40 % and 8 g/l – 74.3 %.

Questions regarding the possible use of "PZF" carrageenan in food products subject to freezing require further research.

9.3.4 Study of the pH effect on the rheological properties of "PZF" carrageenan solutions

The formation of product quality is carried out at all stages of the technological process of its production. Many technological indicators that ensure the creation of a high-quality product depend on the active acidity (pH) of the food system.

Almost every food product has optimal conditions for the cooking process. It is extremely important that the "PZF" carrageenan solution has the necessary rheological properties under these conditions. One of the criteria for the suitability of a solution of a high-molecular compound as a gelling agent is the pH range within which this drug retains its technological and consumer properties.

To study the effect of acidifying agents, 30 % acetic acid was used, which was added to gels with different concentrations to pH 1–2. The pH was monitored using a pH meter.

The most acceptable alkaline agent for the food industry is calcium bicarbonate (baking soda) – the cheapest reagent that creates milder hydrolysis conditions compared to alkalis.

To study the effect of alkaline agents, a 15 % solution of baking soda was used, which was added to gels of various concentrations to a pH of 10–11. The pH was monitored using a pH meter.

Fig. 9.7 shows the dependence of the viscosity of "PZF" carrageenan solutions on pH at a shear rate of 1312 s^{-1} and a temperature of 25 °C.

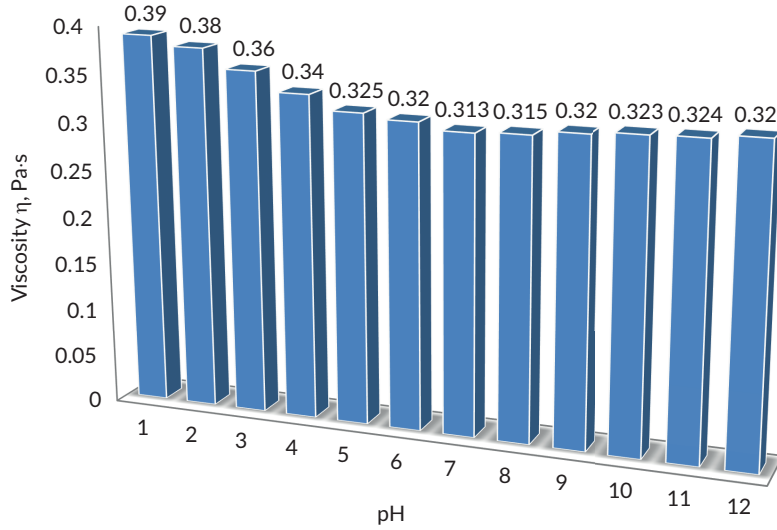

Fig. 9.7 Dependence of viscosity of "PZF" carrageenan solutions on pH

As the pH increases from 1 to 10, the viscosity decreases slightly. In a more alkaline environment, the viscosity of the solution drops steeper, probably due to partial ionization of hydroxyl groups of mannose and especially galactose units. In weakly acidic and weakly alkaline environments (pH = 5–8.5), the viscosity varies within relatively small limits (no more than 0.009 Pa·s). With an increase in alkalinity up to pH = 9.5–10, the viscosity of the "PZF" carrageenan solution remains almost at the previous level.

As the acidity of the environment increases, the viscosity of "PZF" carrageenan-based solutions increases significantly. An increase in the concentration of hydrogen ions complicates the dissociation of groups that give macromolecules a negative charge (sulfoether groups). A decrease in the dissociation degree reduces the mutual repulsion of polyanions, contributing to the formation of intermolecular bonds and increasing viscosity. "PZF" carrageenan retains abnormally viscous properties in a strongly acidic environment, up to pH = 1.

A study of the effect of pH on the stability of viscous solutions of "PZF" carrageenan during storage was of some practical interest.

Experimental data characterizing the dependence of the viscosity of "PZF" carrageenan solutions on the storage time at 25 °C are shown in **Table 9.3**.

Table 9.3 Viscosity of carrageenan solutions during storage

Storage time, hours	Viscosity, % of the initial value				
	pH = 2	pH = 4	pH = 6	pH = 7	pH = 10
0	100	100	100	100	100
12	102.1	101.6	100.9	100.9	100.2
24	102.8	103.3	102.1	101.5	101.8
36	103.9	105.2	104.8	104.9	105.6
42	103.6	105.8	105.1	105.3	106.5
48	102.7	105.9	105.5	105.4	106.5
54	102.1	106.2	105.3	104.9	106.2
60	100.8	106.7	105	104.8	104.6
66	99.5	106.7	104.7	104.4	104.4
72	98.3	106.9	104.2	103.9	104.4
78	97.6	106.9	103	102.7	104.1
84	95.4	106.8	102.3	100.3	103.3
90	94.5	105.5	100.1	97.5	102.1
90	92.5	104.7	97.8	96.3	99.6
102	89.9	103.6	97.1	93.5	97.5
108	87.5	103.1	94.7	92.2	96
114	85	101.9	92.7	89.1	94.2
120	82.9	99.7	91.5	86.6	92.5
132	77.4	97.3	83.9	83.1	88.4
144	74.1	95.1	82.3	77.5	86
156	69.7	93.1	78.2	73.3	83
168	65.8	92.3	74.7	67.6	80.2

The viscosity of "PZF" carrageenan solutions 1 hour after preparation is taken as 100 %. In the process of storage, the viscosity of the solutions first increased, and then decreased, regardless of the pH value. The increase in viscosity at the initial stage can possibly be explained by some increase in the concentration of "PZF" carrageenan due to the partial evaporation of water from the viscous solution. The subsequent decrease in viscosity is most likely caused by the hydrolysis of carrageenan.

The fastest, after 1.5–2 days, the viscosity of "PZF" carrageenan solutions begins to decrease at pH = 2. Clots with a neutral and alkaline reaction environment fully retain their rheological properties during 3–3.5 days of storage. A week after preparation, the "PZF" carrageenan solution loses up to 30 % of its initial viscosity. A solution with pH = 4 has high stability during storage. An acidic environment prevents the development of microorganisms, however, in this case, it is not strong enough to cause noticeable hydrolysis of the polysaccharide.

Conclusion

1. The technological aspects of the use of carrageenan from the Black Sea red algae "Phyllophora Brody" are substantiated. It is shown that the use of such a drug ("PZF" carrageenan) is expedient for expanding the range of consistency regulators of food industry products.

2. The concentration dependence of the viscosity of "PZF" carrageenan solutions is studied. With an increase in the concentration of "PZF" carrageenan to 2 %, the flow index of the solution decreases sharply, which indicates an increase in the structure of the system.

3. The dependence of the viscosity of "PZF" carrageenan solutions on the shear rate gradient in the interval 3–1312 s^{-1} is established. In the studied range of shear rates, the viscosity of solutions obeys the power law and is described by the Ostwald-Weyl equation. Reversible destruction of the structure occurs under the action of shear. The degree of thixotropic reduction of "PZF" carrageenan solution is 87.9 %.

4. The effect of temperature on the rheological properties of "PZF" carrageenan solutions is studied. It is assumed that at temperatures up to 45 °C, carrageenan macromolecules exist in a spiral conformation, and at higher temperatures undergo a thermoreversible transition into a coil conformation. This transition causes a decrease in viscosity and gelation of the solution.

5. It is established that "PZF" carrageenan solutions retain their abnormally viscous properties in a wide pH range. When the pH of the solution changes

from 1 to 11, no signs of a conformational transition of "PZF" carrageenan macromolecules are detected.

6. The obtained data on the chemical and physical-mechanical properties of "PZF" carrageenan solutions indicate the expediency of continuing research with the aim of forming viscous solutions for structured food products with the expansion of their functional purpose.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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