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STUDY OF THE SPHERIFICATION PROCESS OF CHERRY JUICE

This article investigates the spherification process of cherry juice, a promising direction within molecular gastronomy that has evolved over recent decades from a tool for creating visual and textural illusions into a rigorous scientific discipline integrating biotechnology, physical chemistry, and nutrition science. Microencapsulation via spherification preserves thermolabile bioactive compounds of fruit and berry raw materials, particularly anthocyanins and polyphenols abundant in cherry, a fruit traditional to Ukrainian cuisine, without the degradation typical of classical thermal processing. The relevance of this work stems from the broader paradigm shift in the food industry and restaurant business toward integrating healthy-eating principles into aesthetically distinctive functional culinary products.

The purpose of the study was to investigate the direct spherification of "Shpanka" cherry juice and to substantiate the influence of technological factors – gelation time, thermal treatment temperature, refrigerated storage conditions, and contact with hydroalcoholic media – on the mechanical strength (elasticity) and organoleptic quality of the resulting spheres.

The research objects were spheres obtained by direct spherification of frozen, freshly-pressed cherry juice using sodium alginate (0.75%) and calcium chloride (0.8%); since the organic acids of cherry juice hinder gelation, the initial pH (4.0) was corrected to 4.9 with sodium citrate. Elasticity was calculated as the ratio of instantaneous to maximum deformation.

The optimal exposure time in the coagulation bath was established at 90 s (elasticity 86%); shorter exposure yields a shell unable to withstand load, while longer exposure causes loss of the liquid core. Heating trials (60–90°C) revealed a nonlinear relationship: an initial 10% elasticity drop at 60°C, gradual recovery at 65–75°C, and catastrophic structural failure above 80°C, establishing 75±2°C as the technological optimum (elasticity 84%). Comparative eight-day refrigerated storage (4±1°C) showed that untreated control spheres lost measurable elasticity by day 3–4, with fermentation-related organoleptic signs suggesting microbiological spoilage, whereas heat-treated samples remained stable throughout. Conversely, contact with ethanol solutions (8–16%) produced the opposite effect: elasticity increased due to osmotic dehydration of the alginate gel, indicating potential use as a decorative ingredient in alcoholic beverages.

The findings constitute a comprehensive, experimentally grounded technological protocol for producing spherified cherry juice, applicable to restaurant enterprises seeking to expand functional product offerings based on regional raw materials.

Keywords: *spherification, cherry juice, sodium alginate, molecular gastronomy, elasticity (mechanical strength), functional food products.*

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ДОСЛІДЖЕННЯ ПРОЦЕСУ СФЕРИФІКАЦІЇ ВИШНЕВОГО СОКУ

Стаття присвячена дослідженню процесу сферифікації вишневого соку – перспективного напряму молекулярної гастрономії, яка за останні десятиліття еволюціонувала від інструменту створення візуальних і текстурних ілюзій до строгої наукової дисципліни, що інтегрує принципи біотехнології, фізичної хімії та нутриціології. Мікроенкапсуляція методом сферифікації дає змогу зберегти термолабільні біологічно активні речовини плодово-ягідної сировини – зокрема антоціани та поліфеноли, якими особливо багата вишня, традиційна для української кулінарії культура, – без їхньої деструкції, притаманної класичній термічній обробці. Актуальність роботи зумовлена загальною парадигмальною трансформацією харчової промисловості та ресторанного господарства в напрямі інтеграції принципів здорового харчування у виробництво естетично виразних функціональних кулінарних продуктів.

Метою дослідження стало вивчення процесу прямої сферифікації вишневого соку сорту «Шпанка» та обґрунтування впливу технологічних факторів – тривалості гелеутворення, температури термічної обробки, умов холодильного зберігання й контакту з водно-спиртовим середовищем – на механічну міцність (пружність) і органолептичну якість отриманих сфер.

Об'єктами дослідження слугували сфери, отримані методом прямої сферифікації із замороженого свіжовичавленого вишневого соку з використанням альгінату натрію (0,75 %) та хлориду кальцію (0,8 %). Оскільки вишневий сік містить яблучну, лимонну, хлорогенову, винну та бурштинову кислоти, що ускладнюють гелеутворення, pH вихідної суміші (4,0) коригували цитратом натрію до 4,9. Показник пружності визначали як відношення миттєвої деформації оболонки до максимальної.

Установлено, що оптимальна тривалість експозиції крапель альгінатного розчину в коагуляційній ванні хлориду кальцію, яка контролює кінетику іонотропного гелеутворення за моделлю «яєчної коробки», становить 90 с (пружність 86 %); за меншої тривалості оболонка не витримує навантаження, за більшої – втрачається рідке ядро сфери. Дослідження впливу нагрівання (60...90 °С) на міцність сфер виявило нелінійну залежність: початкове зниження пружності на 10 % за 60 °С змінюється поступовим відновленням показника в діапазоні 65...75 °С і катастрофічним руйнуванням структурної цілісності за температур понад 80 °С, що дало підстави визначити технологічний оптимум нагрівання – 75 ± 2 °С (пружність 84 %).

Порівняльний аналіз восьмидобового холодильного зберігання (4 ± 1 °С) контрольного (ненагрітого) і термічно оброблених зразків засвідчив вирішальну роль попередньої термообробки: контрольний зразок утратив вимірювану пружність уже на 3–4-ту добу, а органолептичні ознаки бродіння (сторонній запах, газоутворення, розчинення оболонки) вказали на ймовірну мікробіологічну природу псування, тоді як нагріті зразки зберігали цілісність і задовільні показники впродовж усього терміну спостереження. Водночас контакт сфер із розчинами етанолу (8...16 %) упродовж 2–12 хв демонстрував протилежний ефект – закономірне зростання пружності внаслідок *осмотичного зневоднення альгінатного гелю, що відкриває перспективу застосування продукту як стабільного декоративного інгредієнта алкогольних напоїв.*

Отримані результати формують цілісний, експериментально обґрунтований технологічний регламент виробництва сферифікованого вишневого соку – від корекції сировини через параметри гелеутворення й термічного оброблення до умов зберігання та специфічного застосування, – придатний для практичного впровадження на підприємствах ресторанного господарства, зацікавлених у розширенні асортименту функціональних страв на основі регіональної сировини.
Ключові слова: *сферифікація, вишневий сік, альгінат натрію, молекулярна гастрономія, пружність (механічна міцність), функціональні продукти харчування.*

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Problem statement in general form and its connection with important scientific or practical tasks

The modern food industry and the restaurant sector are undergoing a paradigm shift, driven by the need to integrate the principles of healthy eating into the processes of creating high-quality culinary products. Molecular gastronomy, which in its early stages of development in the 1980s was perceived primarily as an avant-garde tool for creating visual and textural illusions, has now evolved into a scientific discipline. This evolution is characterised by the integration of principles from biotechnology, physical chemistry, rheology and nutrition science, with the aim of creating innovative food products that offer high physiological and dietary value for the human body [1].

Research shows that controlled manipulation of texture and aroma through molecular gastronomy techniques influences consumer satisfaction and their emotional responses, giving rise to a new field – neurogastronomy. The fundamental basis of modern molecular gastronomy lies in an understanding of the physico-chemical transformations that occur in food ingredients at the molecular level under the influence of various thermal, mechanical and chemical factors [2].

One of the most promising areas in this field, which is attracting increasing attention from scientists and chefs alike, is the microencapsulation of bioactive substances using spherification techniques. Instead of using artificial syrups or synthetic colourings, the current gastronomic trend focuses on the use of exclusively natural products – in particular, freshly squeezed fruit, berry and vegetable juices, as well as herbal extracts [3].

This approach makes it possible to transform gourmet dishes into fully-fledged functional foods, enriched with polyphenols, vitamins, natural antioxidants and probiotic cultures [4]. Thanks to microencapsulation, these heat-labile and oxidation-sensitive compounds retain their biological activity throughout all stages of culinary processing and digestion.

In modern molecular gastronomy, two main methods of spherification are used: direct (basic) and reverse. The choice of a specific method depends critically on the biochemical composition of the raw material, its acidity and the presence of endogenous calcium [5].

To improve the rheological properties of the membrane and prevent mass loss of the spheres (syneresis) during storage, the latest modifications to the process have been developed. According to research, the addition of xanthan gum or agar-agar to the liquid core significantly optimises the hydrodynamic characteristics of the microcapsules. Due to the increased viscosity of the liquid at the centre of the sphere, the rate of diffusion of water and dissolved substances through the porous calcium alginate membrane is significantly reduced, which is consistent with Poiseuille's law for fluid flow through capillaries [6].

One of the main challenges in traditional cooking is the inevitable loss of heat-labile nutrients (vitamins, antioxidants, enzymes) during the heat treatment of food. Molecular techniques, in particular spherification, take place exclusively at room temperature or below, ensuring maximum preservation of the phytochemicals, polyphenols and macronutrients contained in natural juices [7]. The innovative concept of microencapsulation enables the creation of products that act as biological delivery vectors, transporting beneficial substances directly into the gastrointestinal tract.

The use of fresh fruit, berry and vegetable juices, as well as plant extracts, as the base liquid for spherification creates a new-generation product: a semi-permeable alginate shell protects the bioactive substances in the liquid core from premature oxidation caused by molecular oxygen, light and aggressive enzymes [8].

Scientific research in recent years has demonstrated the successful use of various natural juices in microencapsulation processes:

Firstly, the microencapsulation of tomato juice. Tomatoes are rich in lycopene (a powerful carotenoid antioxidant) and ascorbic acid (vitamin C). The use of reverse spherification methods with calcium lactate allows the creation of functional 'tomato caviar', which successfully preserves the levels of β-carotene. However, the process requires strict control of pH and temperature, as vitamin C is extremely susceptible to degradation during prolonged processing [9]. Such spheres are used as highly nutritious garnishes for 'Caprese'-style salads, adding both a unique texture and a concentrated dose of antioxidants.

Secondly, the development of probiotic delivery systems based on orange juice. Spherification serves as a reliable method for delivering live microorganisms, eliminating the need to use dairy products as traditional carriers. An optimised formulation (using the Box-Benken design), comprising 2.98% sodium alginate and 2.87% calcium lactate with a setting time of 40 minutes, enables the effective encapsulation of Lactiplantibacillus plantarum strains in a natural orange juice matrix [10]. The encapsulation efficiency reaches almost 84 per cent. The alginate membrane protects the probiotics from the lethal effects of the low pH of gastric juice, ensuring their controlled release only in the slightly alkaline environment of the small intestine.

Thirdly, the use of pomegranate and cherry juices. These products are characterised by a high content of anthocyanins and ellagitannins, which are sensitive to heat. They are ideal candidates for reverse spherification, as the high acidity of the juice is compensated for by the technique of immersion in a neutral alginate bath. The resulting microcapsules are used as natural antioxidant additives capable of replacing synthetic preservatives in functional drinks and desserts [11].

A separate promising area of research involves the spherification of extracts from oolong tea, hibiscus (Hibiscus sabdariffa L.) and myrtle leaves (Myrtus communis L.). These phytoextracts are used to create capsules with antioxidant potential (as confirmed by ABTS and DPPH assays). Thanks to the microporous structure of calcium alginate, such spheres are capable of releasing catechins and other polyphenols in a controlled manner over a period of 48 hours, ensuring a prolonged therapeutic effect and preventing lipid oxidation in complex food systems [12].

It can therefore be concluded that the modern food industry is undergoing a paradigm shift, driven by the need to integrate the principles of healthy eating into food production technologies. The microencapsulation of bioactive substances using the spherification method [3] is becoming particularly relevant, as traditional heat treatment destroys heat-labile polyphenols, vitamins and antioxidants in natural raw materials, whereas molecular techniques preserve them by carrying out the process at room temperature [7].

Most natural juices are characterised by a high content of biologically valuable but heat-sensitive compounds [13]. Therefore, determining the optimal technological parameters for spherification of this particular raw material is a pressing scientific challenge, the resolution of which is of practical importance for the development of functional drinks and desserts with natural antioxidant activity as an alternative to synthetic preservatives.

Analysis of recent research and publications

Among the variety of molecular gastronomy techniques, spherification occupies a special place as a process of controlled ionotropic gelation, which allows liquids to be encapsulated within a thin, semi-permeable hydrocolloid membrane [14]. The fundamental basis of this technology is the use of alginates – linear anionic polysaccharides extracted from brown seaweeds (Phaeophyceae) [15].

The current state of research in this field demonstrates a paradigm shift: spherification has evolved from a purely hedonistic tool for creating visual effects (‘artificial caviar’) in haute cuisine restaurants to a biotechnological platform for developing functional products [16].

This transition is largely driven by global shifts in consumer demand. According to market analysis of hydrocolloids, there is a sustained demand for ‘clean label’ products, where synthetic thickeners are replaced by natural alternatives of biogenic origin [17]. Alginates, alongside pectins and carrageenans, are ideally suited to these requirements, providing structural stabilisation and acting as prebiotic fibres in the gastrointestinal tract [18].

Despite its commercial appeal, the wider use of spherification in food technology faces a number of challenges. The raw material supply for alginates depends on the volatility of seaweed harvests and climate change, whilst stringent regulatory standards require thorough scientific justification of the safety and efficacy of encapsulating novel food matrices [17]. Consequently, a detailed analysis of the spherification processes of various food matrices – ranging from natural juices with their complex acidity to concentrated syrups and dairy emulsions – is emerging as one of the priority tasks of modern food engineering.

Against the backdrop of global growth in demand for functional foods, research into the spherification of natural juices is becoming increasingly relevant. Natural juices and extracts from plant-based raw materials contain a rich spectrum of heat-labile antioxidants, flavonoids and organic acids, which degrade easily under the influence of light, oxygen or the aggressive acidic environment of the gastrointestinal tract [19].

Converting liquid juice into spheres using alginate hydrogels creates a reliable physical and chemical barrier to protect valuable nutrients. Research into the spherification of broccoli sprout juice, which is a source of sulforaphane, has yielded significant results. The incorporation of additional polysaccharides – pectin, κ -carrageenan, gum arabic and konjac glucomannan – into the alginate matrix enabled the creation of composite membranes with an encapsulation efficiency of up to 61,93 per cent. These gel spheres (BSJAB) exhibited marked gastro-resistance: thanks to their increased structural density, they significantly reduced their shrinkage in simulated gastric juice, limiting the premature release of sulforaphane to less than 40 per cent. Upon entering the alkaline environment of simulated intestinal fluid, the matrix gradually degraded, ensuring over 80% release of the bioactive compound in the zone of maximum absorption [20].

Similar mechanisms were investigated during the encapsulation of anthocyanins from purple sweet potato extract into spheres based on konjac glucomannan and sodium alginate [20]. It has been demonstrated that the microstructure of such spheres ensures reliable retention of water molecules, modulates the kinetics of anthocyanin release in vitro, and preserves their high antioxidant capacity over a prolonged storage period [21].

The incorporation of jujube (marmalade tree) extract into complex alginate matrices (Al-IFPG), enriched with whey and pea protein isolates, revealed a synergistic effect of protein-carbohydrate interaction. The presence of protein in the capsule structure triggered the formation of intramolecular β-folded structures, confirmed by Fourier-transform infrared (FTIR) spectroscopy, which significantly increased the glass transition temperature (T_g to 77,23°C) and ensured unprecedented thermal stability of the product [22].

The development of pH-sensitive bilayer hydrogels is another promising approach to addressing the problem of low bioavailability of extracts. Researchers have developed a ‘core-shell’ system based on sodium alginate and carboxymethylcellulose for the delivery of chlorogenic acid. This bilayer barrier inhibited the release of the active substance in the aggressive gastric environment (pH 1,2), limiting losses to 30 per cent, whilst ensuring prolonged, controlled release (approximately 70% over 10 hours) in the intestinal tract (pH 6,8) [21].

Despite the proven effectiveness of encapsulation, the spherification of natural juices is complicated by their marked heterogeneity. Many fruit and berry juices (particularly apple, citrus and cranberry juices) contain high concentrations of endogenous pectin and organic acids. The presence of D-gluconic acid, which occurs naturally in fruit juices, grapes, apples and wine, acts as a complexing agent. Gluconates are capable of binding divalent cations, forming strong chelate complexes, which prevents the formation of calcium phosphates and the clouding of the juice. However, during the reverse spherification process, this ability of gluconic acid leads to competitive binding of calcium ions, preventing their diffusion into the alginate and critically weakening the gel membrane [23].

Furthermore, natural juices often have a pH level that falls outside the optimal range for alginate gel formation. Adjusting the acidity using alkaline buffers often spoils the authentic flavour of the juice, giving it a soapy or salty aftertaste. Resolving these contradictions requires precise modelling. Researchers employ Response Surface Methodology (RSM) to mathematically optimise reagent concentrations. In particular, the use of RSM during the development of liquid-core hydrogel beads containing functional compounds derived from radish by-products enabled the precise determination of the ideal process parameters: the time of initial gel formation (23.99 min) and the concentration of calcium lactate (0,13 M), which ensured a shell hardness of 25,5 N and high polyphenol retention efficiency [24].

The encapsulation of media with high sugar concentrations – such as syrups, fruit compotes, honey and caramel sauces – presents specific rheological and osmotic challenges. Honey and syrup matrices are characterised by extremely high density. When these are introduced dropwise into an alginate solution (in the reverse spherification paradigm), gravitational forces significantly outweigh surface tension forces. As a result, the droplet does not have time to assume a spherical shape before cross-linking begins and transforms into an elongated capsule with a characteristic 'tail' or a shapeless clot [25].

To stabilise the hydrodynamic behaviour of syrups, food engineers and technologists employ rheological modifiers, in particular xanthan or gellan gum. The addition of xanthan gum in microconcentrations (0,2–0,5%) imparts pseudoplastic fluid properties to the syrup. This ensures high viscosity of the system at rest, allowing the droplets to retain their spherical shape when immersed in the bath, whilst not hindering the diffusion of calcium ions required for membrane formation [26]. Gellan gum, in turn, has demonstrated the ability to enhance the mucoadhesive properties of the spheres and ensure prolonged release of active substances, as demonstrated during the optimisation of microgranules containing vildagliptin [27].

Another obstacle is the high osmotic pressure inside the syrup sphere. The high concentration of solutes within the encapsulate causes water to diffuse from the alginate solution or the surrounding aqueous medium into the sphere. This process of osmotic swelling dilutes the flavour of the syrup and, in critical cases, leads to the rupture of the alginate shell. An alternative way of addressing the problem of high osmotic pressure in carbohydrate-based syrups is to switch to low-calorie sweeteners. Studies of liquids containing stevia extracts have shown that such solutions allow stable spheres to be formed without adverse osmotic effects. Stevia-based spheres demonstrated excellent physicochemical properties, retained their authentic colour and ensured high microbiological purity for at least 7 days of storage [28].

In addition to culinary applications, the encapsulation of sugar alcohols (mannitol and sorbitol) in alginate matrices is widely used in biotechnology for the cryopreservation and long-term storage of plant tissue cultures. In this case, polyols function not only as a source of energy but also as osmotically active regulators and free radical scavengers, ensuring high cell viability after encapsulation [29].

Despite the rapid development of research in the field of molecular gastronomy, the industrialisation of spherification processes still faces a number of fundamental and technological challenges, which will shape the direction of scientific research in the coming years.

One of the key obstacles remains the long-term thermodynamic instability of calcium alginate gels: the three-dimensional polymer network continues to compact over time, displacing the encapsulated moisture along with the nutrients dissolved in it, causing the spheres to shrink and lose their visual appeal. Slowing down this synergetic process through the coacervation of alginate with other hydrocolloids currently presents a significant challenge for materials scientists [30].

An equally significant challenge is the inherent heterogeneity of plant-based raw materials: natural fruit and vegetable juices are chemically unstable systems in which the content of endogenous pectins, minerals and organic acids varies depending on the terroir, the plant variety and the climatic conditions at the time of harvest. The lack of a stable composition makes it impossible to develop a universal algorithm for direct or reverse spherification suitable for any juice; consequently, each new batch of raw material requires separate titration of the buffer capacity and recalculation of reagent concentrations, which significantly complicates the transition to mass production [31].

The issue of bioavailability of the encapsulated compounds deserves special attention. The mechanical strength of the alginate membrane has both positive and negative effects on the product's functionality: dense cross-linking provides reliable protection for probiotic cultures and antioxidants as they pass through the gastric environment, whilst excessive stiffness of the matrix can hinder its enzymatic degradation in the small intestine, blocking the release and absorption of valuable metabolites. Establishing the optimal balance between the barrier properties of the coating and its biodegradability requires long-term in vivo clinical studies [32].

Industrial upscaling of the process also remains a significant technological challenge: the vast majority of existing studies rely on laboratory methods of droplet dosing using syringes, pipettes or multi-nozzle spoons [33], whereas transferring these approaches to industrial extrusion lines is accompanied by droplet coalescence before gelation is complete, hydrodynamic deformation during the fall into large-volume reactors, and difficulties in the continuous separation and rinsing of fragile capsules without compromising their integrity [34].

At the same time, accumulated research findings on the encapsulation of microorganisms – in particular, the nematode Steinernema feltiae in combination with plant extracts for agrobiotechnology applications, as well as the stabilisation of cultures for nuclear magnetic resonance studies – demonstrate the high biocompatibility of alginate matrices. However, the interaction of hydrocolloids with the latest types of food carriers, such as plant-based meat or emulsion systems like Go!Drop (water-in-oil), requires further study of the associated phase transitions [35].

Formulation of the article's objectives

A review of the literature indicates that, in the preparation of dishes at catering establishments and in food production, spherification techniques are becoming increasingly relevant; these enable the production of spheres from regional plant-based raw materials – berry and fruit juices – and thereby allow consumers to experience local cuisine regardless of the seasonality of the raw materials. Cherries occupy a special place among these raw materials – a crop traditionally used in Ukrainian cuisine and characterised by a high content of polyphenolic compounds, vitamins and other biologically active substances [36]. In view of the above, the aim of this study was to investigate the spherification process of cherry juice and the influence of technological factors on the strength and shelf life of the resulting spheres.

Presentation of the main research material

Materials and methods. The study involved spheres produced by direct spherification using frozen, freshly squeezed 'Shpanka' cherry juice, calcium chloride and sodium alginate, all of which met regulatory safety requirements.

The flavouring solution was prepared by mixing cherry juice with water in a 1:1 ratio; sodium citrate (0.5 per cent by mass of the solution) was used to adjust the pH, after which sodium alginate (0.75 per cent) was uniformly dissolved using an immersion blender. After allowing the mixture to stand and cool (to remove air bubbles), the droplets were immersed in a 0.8 per cent calcium chloride solution for 0.5, 1, 1.5 and 2 minutes – in order to determine the optimal time for shell formation. The resulting spheres were immersed in water and heated to temperatures of 65, 70, 75, 80, 85 and 90 °C.

To investigate the effect of alcohol, two types of samples were prepared – those heated to 75 °C and those left unheated; the eggs were immersed in alcohol solutions with concentrations of 8, 12 and 16 per cent for 2, 4, 6, 8, 10 and 12 minutes. The samples were placed in cold storage at a temperature of 4 ± 1 °C: the control sample (unheated) was placed in a flavouring liquid that had been preheated to 100 °C and then cooled; test samples 1 and 2 (heated to 75 °C) were placed in airtight containers. Specimen 1 was placed without flavouring liquid, whilst specimen 2 was placed in the preheated and cooled flavouring liquid, after which the containers were tightly sealed.

The firmness of the spheres (as measured by the firmness index) and the organoleptic characteristics were determined for all samples. Firmness (U, %) was calculated using the following formula:

$$\sigma = \varepsilon_0 / \varepsilon_{\text{м}} \times 100\% \quad (1)$$

where ε_0 is the instantaneous strain ($\times 10^{-3}$ m), and $\varepsilon_{\text{м}}$ is the maximum strain after 3 minutes ($\times 10^{-3}$ m). Statistical analysis of the results was carried out using Microsoft Office.

Presentation of the main material. When preparing the liquid for encapsulation, it was taken into account that the alginate shell forms stably in a medium with a pH between 5 and 12, as the hydration of sodium alginate in a medium with a pH below 3.6 is difficult or impossible, since sodium alginate is converted into insoluble alginic acid [37]. As highly acidic vegetable or fruit juices are usually used as raw materials for the spheres, the pH is adjusted to 4,6–4,7 using an acidity regulator (sodium citrate). Cherry juice, chosen as a traditional culinary raw material in Ukraine, contains malic, citric, chlorogenic, tartaric, succinic and other acids, which lower the pH and adversely affect gel formation. The initial mixture of cherry juice and water (1:1) had a pH of 4,0; after the addition of sodium citrate, the pH of the solution was raised to 4,9.

The duration of exposure of the alginate solution droplets in the calcium chloride coagulation bath is a key process parameter in direct spheronisation, as it regulates the kinetics of ionotropic gel formation – the diffusion-controlled cross-linking of sodium alginate chains by divalent Ca^{2+} cations according to the classical 'egg-box' model, localised predominantly in the α-L-guluronic acid blocks of the polymer chain. The thickness and mechanical integrity of the resulting gel membrane, which ensures the stability of the product's spherical shape without subsequent sticking or deformation, are directly dependent on the duration of calcium cation diffusion into the volume of the droplet. At the same time, exceeding the optimal exposure time causes the gelation front to progressively advance towards the geometric centre of the droplet, which ultimately leads to the complete conversion of the liquid content into a gel due to the depletion of free carboxyl groups in the alginate and the loss of the liquid core characteristic of a sphere. Quantitative results illustrating this relationship are presented in Table 1.

The results of the study indicate that exposure of the dispersed phase to a calcium chloride solution for more than 60 seconds results in the formation of spherical capsules with a dense gel shell and a liquid core. Increasing the exposure time to over 120 seconds led to a deterioration in the organoleptic properties; consequently, such samples were excluded from the experiment. Optimal rheological characteristics, in particular elasticity indices, were recorded for model systems with an exposure time of 90 seconds. It was these samples that were selected for further investigation of the effect of heat treatment on the mechanical strength and stability of the capsules during storage.

Table 1

Effect of the dwell time of spheres in a calcium chloride solution on their elasticity

Soaking time, s	Instantaneous deformation, $\times10^{-3}$ m	Maximum deformation, $\times10^{-3}$ m	Elasticity, %	Organoleptic assessment
30	–	–	–	The sphere cannot withstand the pressure; the membrane ruptures.
60	1.3 ± 0.1	2.2 ± 0.1	59	The sphere retains its shape well; a flavouring liquid is present in the centre.
90	1.9 ± 0.1	2.2 ± 0.05	86	The sphere retains its shape well, with flavouring liquid present in the centre.
120	–	–	–	A thick gel-like shell; when bitten into, it feels like pieces of jelly; there is practically no flavouring liquid in the centre.
150	–	–	–	A thick gelatinous coating; when chewed, it feels like small pieces of jelly.

In the second stage of the study, the effect of heat treatment on the mechanical strength of spherical capsules during heating (Table 2) and their structural stability during subsequent storage was analysed.

Analysis of the data presented in Table 2 shows that, at the initial stage of heat treatment, the mechanical strength of the alginate membrane decreases by 10 per cent. At the same time, within the temperature range of 65–75 °C, a gradual recovery of elastic properties to a level close to the initial value is observed. Upon reaching 80 ± 1 °C, the capsules lose their spatial configuration, and their structural integrity becomes insufficient to withstand the load during the determination of the yield point. Exposure to temperatures above 85 °C causes the samples to turn into a paste-like consistency, lose their spherical shape completely and fail instantly under mechanical stress. The optimum heating temperature has been determined to be 75 ± 2 °C.

The sphere samples obtained under optimised spherification conditions were placed in cold storage at 4 ± 1 °C. The control sample (without heating) was placed in flavouring liquid that had been preheated to 100 °C and then cooled; experimental samples 1 (without flavouring liquid) and 2 (with flavouring liquid that had been preheated to 75 ± 2 °C and then cooled) were placed in airtight containers, which were then tightly sealed. They were subsequently stored for 8 days. During storage, organoleptic parameters (Table 3) and changes in the elasticity index (Fig. 1) were recorded daily. The elasticity index decreased throughout the entire storage period; however, the heated spheres retained their integrity and shape during measurement. In contrast, the control (unheated) sample began to lose its ability to withstand the load during the determination of maximum deformation as early as the third day of storage – the shell ruptured. On the fourth day, it was not possible to measure the elasticity of the control sample.

The data in Figure 1 and Table 3, taken together, demonstrate a clear dependence of the spheres' stability on their prior heat treatment. The elasticity curve of the control (unheated) sample shows the sharpest drop in the index and, as early as the third day, falls outside the measurable range due to shell rupture – this is consistent with the organoleptic data in Table 3, where the first (faint) odour of fermentation is recorded from the third day onwards, followed by progressive softening, local ruptures of the casing and the almost complete dissolution of the samples by the 7th–8th day.

Table 2

Effect of heating temperature on the strength of spheres

Temperature, °C	Instantaneous deformation, $\times10^{-3}$ m	Maximum deformation, $\times10^{-3}$ m	Elasticity, %	Organoleptic assessment
without heating	1.9 ± 0.10	2.2 ± 0.05	86	The sphere retains its shape well, with a flavourful liquid present in the centre.
60	1.3 ± 0.02	1.8 ± 0.09	76	The sphere retains its shape well; no rupture occurs
65	1.7 ± 0.05	2.2 ± 0.08	79	The egg shell retains its spherical shape; no rupture occurs

Temperature, °C	Instantaneous deformation, ×10⁻³ m	Maximum deformation, ×10⁻³ m	Elasticity, %	Organoleptic assessment
70	2.3 ± 0.01	2.8 ± 0.10	82	The egg shell retains its spherical shape; no rupture occurs
75	2.5 ± 0.05	3.0 ± 0.05	84	The egg shell retains its spherical shape; no rupture occurs
80	1.1 ± 0.03	–	0	The sphere cannot withstand the load required to determine the maximum deformation; the shell ruptures
85	–	–	0	The sphere cannot withstand the load; the shell ruptures
90	–	–	0	The sphere cannot withstand the load; the shell ruptures

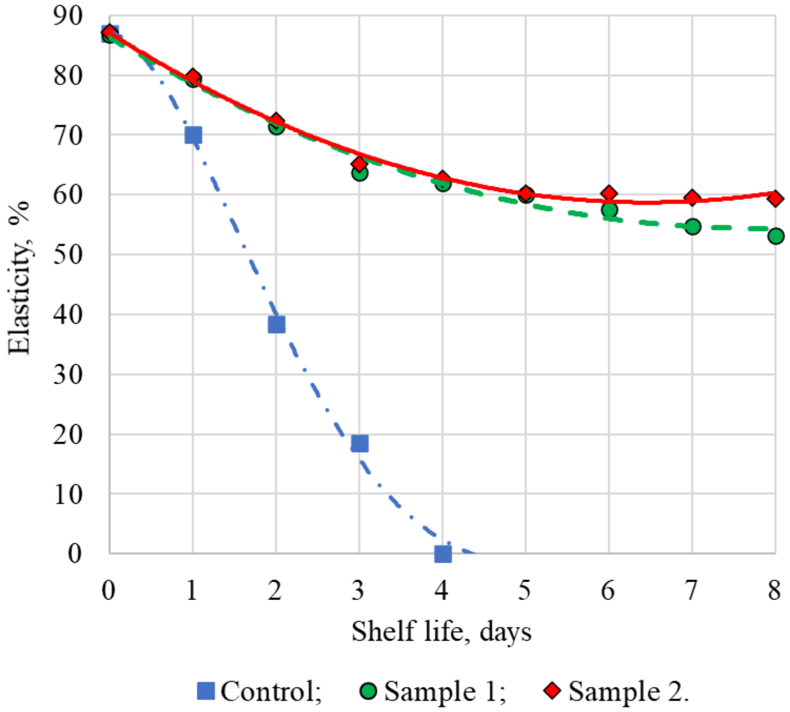

Fig. 1. Change in the elasticity of the samples during storage

In contrast, the curves for samples 1 and 2 (heated to 75 ± 2 °C) decline much more slowly and remain measurable throughout the entire eight-day period; signs of fermentation (isolated bubbles, a barely perceptible odour) in sample 1 only appear from the 6th day onwards, whereas sample 2 (with a pre-heat-treated flavouring liquid) shows no odour of fermentation at all until the 8th day.

This combination of signs – gas formation, the appearance of an off-odour of fermentation and the progressive breakdown of the calcium alginate casing – is a typical indicator of spoilage of a microbiological, rather than purely physico-chemical, nature: organic acids and CO_2, formed during the metabolic activity of residual microflora in the juice (yeasts, heterofermentative lactic acid bacteria), are capable of displacing Ca^{2+} ions from the 'egg carton' structure, weakening the gel network, whilst the internal gas pressure further causes the casing to rupture.

Since the tasting liquid of the control sample had been preheated to 100 °C, just as in sample 2, the decisive protective factor is the heat treatment of the sphere itself (75 ± 2 °C), which reduces the initial microbial load of the raw material; additional treatment of the surrounding liquid (sample 2) provides a further barrier against recontamination.

As the study relied exclusively on organoleptic assessment, to definitively confirm the microbiological nature of the spoilage, it would be advisable to supplement the subsequent stages of the work with direct microbiological testing (total plate count, yeasts and moulds) of the control and test samples.

Table 3

Changes in the organoleptic characteristics of the samples during storage

Day	Sample	Organoleptic characteristics
1	Control	Spherical in shape, intact, with a firm skin; a liquid flavouring fraction is present in the centre; no foreign odours.
	Sample 1	Shape intact, skin firm, liquid centre; no foreign odours (common baseline value for all samples prior to the branching of storage conditions).
	Sample 2	Shape intact, skin elastic, liquid centre; no foreign odours (common baseline value).
2	Inspection	The shape is largely still intact, although the first signs of loss of elasticity have been observed. No odour of fermentation is present.
	Sample 1	The shape is intact, the skin is firm; the flavour and aroma are pronounced, with no off-odours – the fruit is firm.
	Sample 2	The shape is intact, the skin is firm; the flavour and aroma are pronounced, with no off-odours – the condition is firm.
3	Inspection	The casing is softened and does not retain its spherical shape; there is a faint odour of fermentation; air bubbles are present inside.
	Sample 1	The shape is intact; the taste and aroma of cherries are pronounced.
	Sample 2	Shape intact; distinct cherry flavour and aroma.
4	Control	The casing is significantly softened and barely retains its spherical shape; the odour of fermentation intensifies from ‘slight’ to ‘pronounced’, with noticeable localised ruptures in the casings.
	Sample 1	The shape remains intact; the flavour and aroma are gradually weakening – a transitional state between ‘pronounced’ and ‘subdued’.
	Sample 2	The shape remains intact; the cherry aroma weakens slightly – a transitional state between ‘distinct’ and ‘pronounced’.
5	Inspection	The casing is softened and does not retain its shape; the casings have ruptured and partially dissolved in the flavouring liquid; a pronounced smell of fermentation; air bubbles.
	Sample 1	The shape is intact; the flavour and aroma are less pronounced.
	Sample 2	The shape is intact; pronounced cherry flavour and aroma.
6	Inspection	The shells have ruptured and partially dissolved in the flavouring liquid; the smell of fermentation is pronounced or approaching pronounced.
	Sample 1	The shape is still intact; the cherry aroma is weaker than before, with the appearance of a barely perceptible odour of fermentation and isolated air bubbles.
	Sample 2	The shape remains intact; the cherry aroma is present but less intense than at previous stages; based on the current trend, no signs of fermentation are expected.
7	Inspection	The samples have dissolved almost completely in the tasting liquid; there is a pronounced odour of fermentation.
	Sample 1	The shape is intact, with a faint odour of fermentation; air bubbles are present inside.
	Sample 2	The shape is intact; a cherry aroma is present (without any additional characteristics).
8	Assessment	The samples dissolve almost completely in the tasting liquid; there is a pronounced odour of fermentation.
	Sample 1	The shape is still intact; a faint odour of fermentation and isolated bubbles are becoming more noticeable.
	Sample 2	The shape is retained; the cherry aroma is moderate; there is no odour of fermentation.

Figure 2 shows photographs of the control sample and samples 1 and 2 after 4 days of storage.

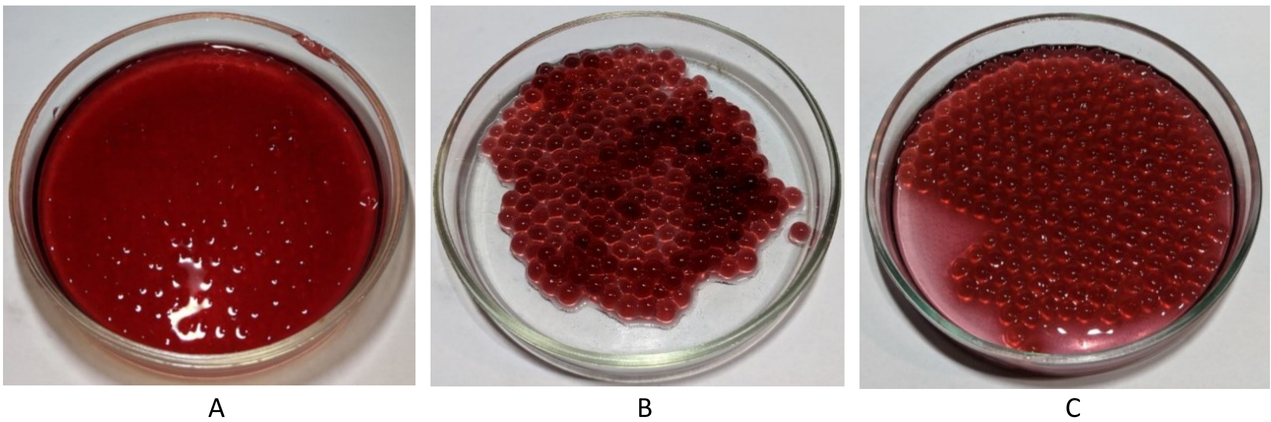

Fig. 2. Appearance of the samples: A – control sample; B – sample 1; C – sample 2.

Given the potential use of spherified cherry juice as a decorative ingredient in alcoholic beverages, the effect of water-alcohol media (with ethanol concentrations of 8, 12 and 16 per cent) for exposure durations of up to 12 minutes on the rheological (elasticity) and organoleptic properties of the capsules. The experimental tests were carried out in a comparative manner for native (unheated) and heat-treated (at 75 °C) samples.

Fig. 3 shows a relationship that is opposite in direction to that observed in the storage data (Fig. 1): in both graphs (A – native samples, B – heat-treated samples), the elasticity index increases with an increase in the mass fraction of ethanol (8→16 %) and the duration of exposure (2→12 min), rather than decreasing, as during cold storage. This increase is purely physico-chemical in nature, rather than microbiological, and is explained by the osmotic dehydration of the calcium alginate gel: ethanol, whilst being hydrophilic but unable to fully solvate the alginate polymer chains, competes with them for bound water molecules, creating a water activity gradient between the gel matrix and the water-alcohol medium. As a result, water diffuses out of the membrane faster than ethanol penetrates inwards, causing the polymer network to contract and increasing the local density of Ca^{2+} cross-links within the 'egg-crate' structure. The compacted, partially dehydrated membrane exhibits faster elastic recovery following instantaneous deformation, which is recorded as an increase in the elasticity index.

A comparison of panels A and B suggests that native (unheated) samples, which contained a greater reserve of free water in the gel prior to testing, demonstrate a more pronounced increase in elasticity, whereas heat-treated spheres, which had already partially lost moisture during heating to 75 ± 2 °C, start from a slightly different baseline and change less abruptly. The practical implication for the intended application (as a decorative ingredient in alcoholic beverages) is ambiguous: on the one hand, the thickening of the shell increases the capsule's mechanical stability in a cocktail; on the other hand, an excessive increase in stiffness at high alcohol concentrations and prolonged exposure risks shifting the texture of the sphere from the desired 'explosive' effect in the mouth to a rubbery one, which should be taken into account when formulating recommendations regarding the optimal contact time between the spheres and the alcoholic beverage prior to serving.

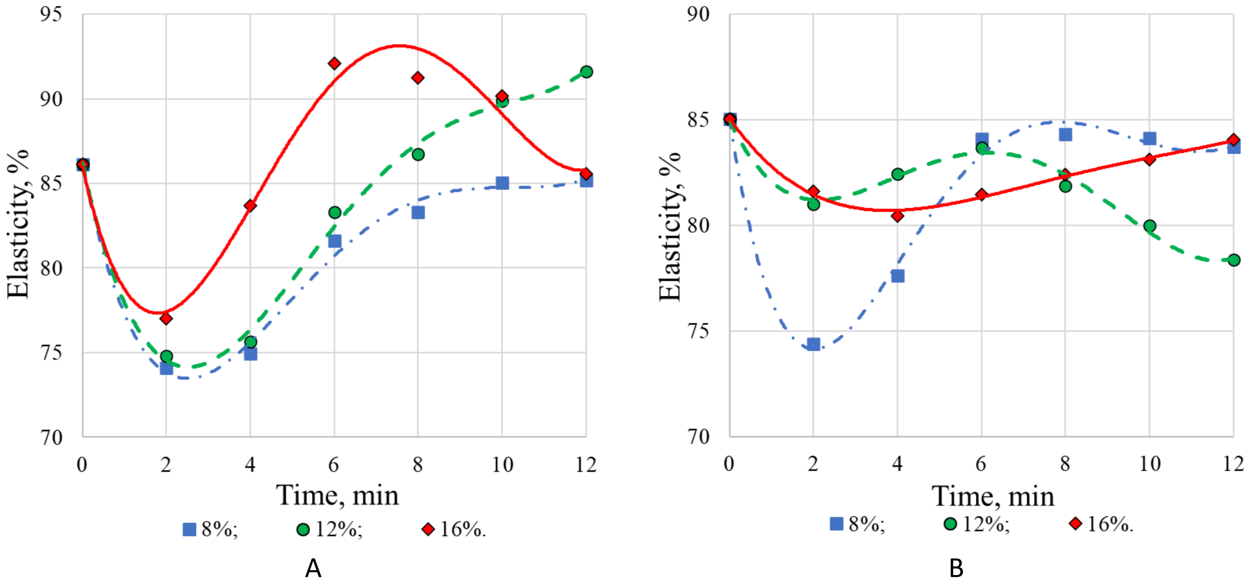

Fig. 3. Effect of alcohol mass fraction and holding time on the elasticity of cherry juice spheres.
A – samples without heat treatment; B – samples treated at 75 ± 2 °C

Conclusions of this research and prospects for further research in this direction

As a result of the study, a technologically sound process for the direct spherification of 'Shpanka' cherry juice has been established, covering all key stages – from the preparation of raw materials to the storage of the finished product.

It has been shown that the initial acidity of the cherry juice (pH 4,0 in a 1:1 mixture with water) is insufficient for the stable hydration of sodium alginate; therefore, adjusting the pH to 4,9 using sodium citrate is an essential technological step. It has been determined that the optimum exposure time for droplets of alginate solution in a calcium chloride coagulation bath is 90 s: at shorter durations (30–60 s), the shell is too thin and cannot withstand mechanical stress, whilst exceeding 120 s causes excessive gel formation, loss of the liquid core and a deterioration in organoleptic properties.

A study of the effect of heat treatment on the mechanical strength of the spheres revealed a non-linear relationship between elasticity and heating temperature: an initial 10 per cent reduction at 60 °C is followed by a gradual recovery in the range 65...75 °C, followed by a loss of structural integrity at temperatures above 80 °C. On this basis, the optimal heating temperature of 75 ± 2 °C was established, which combines a sufficient level of heat treatment with maximum preservation of the shell's elasticity (84 %).

A comparative analysis of the shelf life of the control (unheated) and heat-treated samples during refrigerated storage (4 ± 1 °C, 8 days) confirmed the role of preliminary heat treatment: the control sample lost its measurable elasticity as early as the 3rd or 4th day, accompanied by organoleptic signs of fermentation (off-odour, gas formation, softening and dissolution of the casing), which highly likely indicates the microbiological nature of the spoilage, rather than purely physico-chemical degradation of the gel. In contrast, the heated samples retained their structural integrity and satisfactory organoleptic characteristics throughout the entire eight-day observation period, demonstrating the effectiveness of heat treatment as a means of extending the shelf life of the capsules.

Separately, an opposite effect of the water-alcohol medium was observed: unlike storage, contact of the spheres with ethanol solutions (8–16 %) is accompanied by an increase in the elasticity of the shell proportional to the alcohol concentration and duration of exposure, which is explained by osmotic dehydration of the calcium alginate gel, rather than microbiological or other destructive processes. This opens up the prospect of using spherified cherry juice as a stable decorative ingredient in alcoholic beverages; however, it requires justification of the upper limit on contact time, beyond which excessive compacting of the shell may impair the desired sensory effect of the 'burst' of flavour in the mouth.

Taken together, the results obtained provide a comprehensive technological overview of the production of spherified cherry juice – from the formulation, through gelation parameters and heat treatment, to storage conditions and specific applications in alcoholic beverages – which is of direct practical significance for catering businesses interested in expanding their range of functional and aesthetically striking dishes based on regional ingredients.

Promising areas for further research include direct microbiological confirmation (determination of total microbial count, yeasts and moulds) of the hypothesis regarding the microbial nature of the spoilage of control samples; extending the storage life of heat-treated capsules beyond 8 days to establish the actual shelf life; quantitative assessment of the preservation of biologically active substances in cherries (anthocyanins, polyphenols) during heat treatment and storage using HPLC or spectrophotometric tests (DPPH, ABTS); testing the capsules in actual alcoholic beverages (rather than model water-alcohol solutions) with accompanying sensory evaluation of the optimal serving time; and adapting the laboratory drop-wise method to the conditions of industrial continuous production.

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