

ISSN 2313–5891 (Online)

ISSN 2304–974X (Print)

Ukrainian Food Journal

***Volume 11, Issue 3
2022***

Kyiv

2022

Київ

Ukrainian Food Journal is an international scientific journal that publishes articles of the specialists in the fields of food science, engineering and technology, chemistry, economics and management.

Ukrainian Food Journal – міжнародне наукове періодичне видання для публікації результатів досліджень фахівців у галузі харчової науки, техніки та технології, хімії, економіки і управління.

Ukrainian Food Journal is abstracted and indexed by scientometric databases:

Ukrainian Food Journal індексується наукометричними базами:

Index Copernicus (2012)
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Chemical Abstracts Service Source Index (CASSI) (2016)
FSTA (Food Science and Technology Abstracts) (2018)
Web of Science (Emerging Sources Citation Index) (2018)
Scopus (2022)

Ukrainian Food Journal включено у перелік наукових фахових видань України з технічних наук, категорія А (Наказ Міністерства освіти і науки України № 358 від 15.03.2019)

Editorial office address:

National University
of Food Technologies
68 Volodymyrska str.
Kyiv 01601, **Ukraine**

Адреса редакції:

Національний університет
харчових технологій
вул. Володимирська, 68
Київ 01601, **Україна**

e-mail: ufj_nuft@meta.ua

Scientific Council of the National
University of Food Technologies
approved this issue for publication.
Protocol № 3, 24.11.2022

Рекомендовано вченою радою
Національного університету
харчових технологій.
Протокол № 3 від 24.11.2022

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Ukrainian Food Journal is open access journal published by the National University of Food Technologies (Kyiv, Ukraine). The Journal publishes original research articles, short communications, review papers, news and literature reviews dealing with all aspects of the food science, technology, engineering, nutrition, food chemistry, economics and management.

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4 issues per year (March, June, September, December).

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Effect of natural ingredients on the structural-mechanical and physicochemical properties of ice cream mixes

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Abstract

Keywords:

Ice cream
B-glucan
Pectin
Viscosity
Water activity
Surface tension.

Introduction. The purpose of the work was to study the functional and technological properties of natural ingredients in low-calorie ice cream as potential structure stabilizers and fat substitutes.

Materials and methods. Ice cream mixes with β -glucans from oats and yeast, with fermented and non-fermented pectin-containing beet purée were studied. The viscosity of the mixes was measured on an ultrasonic viscometer Unipan type 505, viscoelastic properties on a Kinexus lab+ device, surface tension on a KSV Sigma 700 tensiometer, water activity on an AWM-10 device.

Results and discussion. According to the results of the research, it was established that oat β -glucan shows greater technological activity in the composition of ice cream mixes with a low fat content (2%), compared to β -glucan from yeast, including the combination with soluble pectin of vegetable purée. Fermented beet purée, which contains at least 1.0% soluble pectin, has the greatest impact on the structural and mechanical characteristics of low-fat ice cream mixes in all its combinations with other structuring ingredients. Ice cream mixes with oat β -glucan and vegetable purée at lower frequencies of measurement of viscoelastic properties show high elasticity, but after exceeding a certain frequency value, the structure is destroyed and the mixes show greater viscosity than elasticity, which will allow more intense saturation of the mixes with air under freezing. A correlation between viscosity, water activity and surface tension of low-fat ice cream mixes was revealed, which is explained by intermolecular interaction between macromolecules of hydrocolloids and active binding of free water by a complex of low- and high-molecular compounds. An alternative substitute for the Vianoks C45 stabilization system (mono- and diglycerides of fatty acids + polysaccharides) in the amount of 0.5% in low-fat ice cream is a complex of natural ingredients - oat β -glucan and fermented beetroot purée in amounts of 0.5 and 15%, respectively.

Conclusions. β -glucan from oat and fermented vegetable purée reveal synergism between β -glucan macromolecules and vegetable pectin to form complex three-dimensional structures in low-fat ice cream mixes that significantly improve the viscoelastic characteristics, surface tension, and water activity of the obtained ice cream mixes.

Article history:

Received
12.04.2022
Received in
revised form
25.08.2022
Accepted
1.12.2022

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DOI:

10.24263/2304-
974X-2022-11-3-
3

Introduction

In modern nutrition, there is an increased consumer demand for low-calorie products. Meanwhile, ice cream of classic types is a product with a high fat content (10–16%). Therefore, there is a high demand on production of new types of low-fat or non-fat ice cream (McGhee et al., 2015; Wang et al., 2022, Yilsay et al., 2006). An ice cream is treated as a low-fat product when it contains below 5% of fat (Azari-Anpar et al., 2017).

In the process of modifying ice cream recipes, the main task is to obtain a product with a characteristic creamy consistency and high resistance to melting, which is ensured by maintaining a certain balance between the content of free and bound water, the specified values of the cryoscopic temperature and other physicochemical parameters (Raheem et al., 2021).

The ice cream structure is polydisperse and can be identified as a three-component foam consisting of a network of fat globules and ice crystals dispersed in a highly viscous aqueous phase. A three-dimensional network of partially aggregated fat globules is formed during the freezing of ice cream mixes. Such a network of fat globules surrounds the air bubbles, stabilizes the air phase, and thus improves the resistance to melting of the ice cream (Granger et al., 2005). During the production process of low-fat ice cream, the network of fat globules can be either disrupted or completely absent, which negatively affects the texture of the product (Silva Junior et al., 2011). Therefore, fat in ice cream performs important technological functions, in particular, it ensures the formation of a creamy consistency, stabilizes the foam structure, increases the resistance to melting, and counteracts the excessive growth of ice crystals (Zhang et al., 2018). Instead, the absence of fat or its low content is the reason for the appearance of a coarse crystalline structure, low overrun, low resistance to melting, and "empty" taste (Akalin et al., 2008; Jardines et al., 2020).

This problem prompts scientists to search for new natural ingredients and compositional systems capable of compensating for the lack of fat in ice cream.

Current state of the problem

According to many authors, the energy value of food products can be reduced by partially replacing fat with polysaccharides that effectively mimic its presence (Javidi et al., 2016). The main function of these compounds is the formation of sensory properties characteristic of full-fat ice cream. Polysaccharides, including guar gum (Javidi et al., 2018), maltodextrin and polydextrose (Güzeler et al., 2011), fructooligosaccharides (Akalin et al., 2008), dietary fibers from cereals and citrus fruits (Soukoulis et al., 2010), starch (Sharma et al., 2017) and β -glucans (Abdel-Haleem and Awad, 2015) are most widely used in ice cream as fat substitutes. Among the polysaccharides listed above, β -glucans are not only capable of simulating the presence of fat, but also exhibit high foaming and stabilizing ability. β -glucans also have positive effects on human health, reducing the risk of diet-dependent diseases such as hyperinsulinemia, hyperlipidemia, weakened immunity (Kanagasabapathy et al., 2013), and osteoporosis (Aljewicz et al., 2018).

β -glucans are natural and non-starch polysaccharides (Nishantha et al., 2018) found in algae, yeast, some bacteria, cereals (wheat, oats, barley), seaweed, and fungi (Du et al., 2019; Ege et al., 2021; Şimşekli et al., 2015). The structure and physicochemical properties of β -glucans, in particular water solubility and structuring ability, depend on the source of origin (Lattimer et al., 2010). Thus, the structure of (1-3) β -glucan isolated from *Euglena gracilis*, a single-celled microalgae, is linear. A linear structure is also characteristic of (1-3) β -glucan and (1-4) β -glucan isolated from barley. (1-6) β -glucan and (1-3) β -glucan isolated from

mushroom *Schizophyllum commune* have both linear and branched structures (Seo et al., 2019). It is known that β -glucans with a high molecular weight are more effective biologically compared to β -glucans with a low molecular weight. However, Lei et al. (2015), found that β -glucans obtained from yeast with a low molecular weight are better immunostimulators and antioxidants compared to β -glucans with a high molecular weight. It is also known that β -glucans with a short chain have greater mobility and the ability to form low-energy bonds with active groups of other macromolecules with subsequent possible rearrangement of the formed associates, which is widely used to obtain pseudoplastic food systems (Mishra, 2020). Therefore, it is obvious that β -glucans of various origins have a positive effect on the physicochemical and sensory properties of structured food products. However, there is no comparative analysis of the functional and technological properties of β -glucans of different origins in food systems with the same chemical composition.

β -glucans have not yet been widely used in food technologies (Khanjani et al., 2022), which is due to insufficient awareness of scientists and manufacturers about their functional and technological properties. Instead, Rezaei et al. (2019) proved the expediency of using β -glucan in the amount of 1-2% in the composition of frozen soy yogurt, the viscosity and overrun of which increased while reducing the resistance to melting. To improve the dimensional stability of the ice cream, it is recommended to prolong the exposure of the mix at low positive temperatures before freezing.

Aljewicz et al. (2020) investigated the effect of highly purified (1-3)(1-4) and (1-3) β -glucans in amounts of 0.5 and 1.0% on the physicochemical characteristics of low-fat ice cream. A significant influence of the structure of β -glucans on the consistency and viscosity index, fluidity, cohesiveness and hardness of ice cream was established. The use of (1-3)(1-4) β -glucan led to a significant decrease, and (1-3) β -glucan to an increase in the hardness of ice cream, although both types of β -glucans effectively mimic milk fat content. Abdel-Haleem and Awad (2015) proved the possibility of replacing 0.4% of carboxymethyl cellulose in low-fat ice cream with the same amount of barley β -glucan, which significantly increased the air content in the product with slight thickening of the mix.

The given research results proved that β -glucans are effective multifunctional ingredients in ice cream, in particular, they structure, increase overrun, affect resistance to melting, and imitate the fat content in the product. However, the authors did not investigate the physical characteristics of the aqueous phase of ice cream with β -glucans. There are also no data on the possibility of complex application of polysaccharides of different types and origins.

Currently, ice cream with pectin-containing raw materials (vegetables, berries, fruits and their processing products) is particularly popular as a multifunctional ingredient (Alfaro-Viquez et al., 2018). Pectin substances of plant raw materials (Cornelia et al., 2019; Koxholt et al., 2001) show foaming, emulsifying and structuring ability. High stabilization of the structure of ice cream is usually achieved by increasing the content of soluble pectin in pectin-containing raw materials (Bezusov et al., 2008) by thermoacidic or enzymatic hydrolysis of protopectin contained in pureed fruits and vegetables (Matsko, 2016; Sukhenko et al., 2012). The stabilizing ability of pectins depends on their molecular weight, structure and content in food systems and physicochemical properties of these systems (Fraeye et al., 2009; 2010).

A number of scientists have proven the possibility of replacing pectin with β -glucan in yogurts (Rinaldi et al., 2015; Sahan et al., 2008), milk gels (Sharafbafi, 2012) and low-fat ice cream (Brennan et al., 2002; Schmidt, 2022). However, the structuring ability of β -glucans in the presence of pectin, particularly in low-fat ice cream, has not been studied. Also, the effectiveness of the functional and technological properties of β -glucans of various origins, in particular their influence on water activity and surface tension in the aqueous phase of low-

fat ice cream mixes, has not been analyzed. The above confirms the relevance of conducting this research.

The purpose of the research is to study the functional and technological properties of natural ingredients in low-calorie ice cream as potential structure stabilizers and fat substitutes.

The objectives of the study:

- to conduct a comparative analysis of the structuring ability of β -glucans of different origins in milk ice cream mixes;
- to investigate the effect of β -glucans on water activity and surface tension of low-fat ice cream;
- to identify the most effective option of using natural structuring ingredients for obtaining ice cream with low fat content, including pectin-containing vegetable filler.

Materials and methods

Preparation of experimental samples of mixes for the production of ice cream

Milk and milk-vegetable mixes were obtained by sequential mixing of the recipe ingredients at a temperature of 40–45 °C, with their subsequent pasteurization at a temperature of 85±2 °C for 2–3 minutes. After that, the mixes were homogenized at a speed of 15 000 rpm using an Unidrive X1000 laboratory homogenizer (Ingenieurbüro CAT M. Zipperer), cooled to a temperature of 4±2 °C, vegetable purées were added (if necessary), mixed for 1–2 min and stored for 12 hours.

Vegetable purée was obtained by grinding blanched pieces of beet using a laboratory homogenizer with cutting knives at a speed of 15 000 rpm for 3 min to obtain a purée with a particle size of no more than 1–2 mm. The vegetable purée was divided into two parts. One part was left unchanged, and the other was fermented with Pectolad brand pectinase (Enzym, Ukraine) with a pectolytic activity of at least 30 units/g. The enzymolysis conditions were as follows: mass fraction of pectinase, 0.1%; temperature, 40 °C; duration, 2 hours; active acidity, 4.0 units of pH. The active acidity of vegetable purées was adjusted with the help of citric acid. After the end of enzymolysis, the enzyme was inactivated by the vegetable purée heating to a temperature of 90 °C without holding. The mass fraction of soluble pectin in fermented purée was at least 1.06% (Sapiga et al., 2021).

Chemical composition of mixes for the production of ice cream:

- mass fraction of total solids, 27.5%;
- mass fraction of fat, 2.0%;
- mass fraction of milk solids non-fat, 10.0%;
- mass fraction of Vianoks C45 stabilization system (composition: mono- and diglycerides of fatty acids (E471), guar gum (E412), locust bean gum (E410), carrageenan (E407), 0.5%;
- mass fraction of sugar, 15.0%;
- mass fraction of β -glucan from oats 70%, (AMULYN, China), 0.5%;
- mass fraction of β -glucan from yeast (*Saccharomyces cerevisiae*) 70%, (GOLDCELL, Brazil), 0.5%;
- mass fraction of table beet purée (non-fermented and fermented), 15.0%.

The mass fraction of β -glucan of 0.5% in the composition of ice cream mixes was chosen in accordance with the recommendations of Aljewicz et al. (2020).

A total of 8 mix samples were prepared:

- **control (C)**: mix of classic composition with Vianoks C45 stabilization system;
- **sample 1**: mix with β -glucan from oats;
- **sample 2**: mix with β -glucan from yeast;
- **sample 3**: mix with Vianoks C45 stabilization system and unfermented vegetable purée;
- **sample 4**: mix with Vianoks C45 stabilization system and fermented vegetable purée;
- **sample 5**: mix with β -glucan from oats and unfermented vegetable purée;
- **sample 6**: a mix with β -glucan from oats and fermented vegetable purée;
- **sample 7**: mix with β -glucan from yeast and unfermented vegetable purée;
- **sample 8**: mix with β -glucan from yeast and fermented vegetable purée.

Research methods

The viscosity of the studied mixtures ($\text{mPa} \times \text{s} \times \text{g} \times \text{cm}^{-3}$) was measured using an ultrasonic viscometer Unipan type 505 (UNIPAN, Warsaw, Poland). Before each measurement, the level of the ultrasonic signal was checked. The measuring probe of the magnetostrictive vibrator was completely placed in the mix. The induced ultrasonic waves were damped by the test material, and the results were displayed as the product of viscosity and density in units of $\text{mPa} \times \text{s} \times \text{g} \times \text{cm}^{-3}$. The viscosity was measured for 10 min at 20 °C (Tomczyńska-Mleko et al., 2014).

The viscoelastic behavior of the test samples was measured using plate geometry on a Kinexus lab+ device (Malvern, UK). Two serrated plates with a diameter of 40 mm (PU40X SW1382 SS and PLS40X S2222 SS, plate–plate configuration) were used to minimize the slippage of the mixes, and the gap between them was 2 mm. Tests were performed in the range of 0.1–10.0 Hz at a strain of 0.01%, and changes in the storage (G') and loss (G'') moduli, as well as the phase angle (δ) were recorded. For comparative analysis of rheological differences between samples, the specified parameters were recorded at a frequency of 1 Hz. The research was carried out at a temperature of 25 °C. The measurement results were registered on a computer in the Kinexus Malvern – rSpace program (Nastaj et al., 2020).

Surface tension was measured using a tensiometer KSV Sigma 700 (KSV Instruments, Ltd., Finland) equipped with a platinum de Nooy ring. The dynamic surface tension was calculated using the Sigma 700 Force software complex. Before each analysis, the de Nooy ring was cleaned with distilled water and dried under a flame (Flook et al., 2022).

Water activity (a_w) was measured using an AWMD-10 water activity meter (NAGY, Gäufelden, Germany) with an accuracy of ± 0.001 a_w unit. Before measurement, the device was calibrated according to a special humidity standard (95% HR). Measurements were made at a temperature of 20 °C (Małeckı et al., 2020).

Charts were drawn using Microsoft Excel 2016, data processing was carried out in Statistics 10.

Results and discussion

At the first stage, the structural and mechanical characteristics of ice cream mixes were investigated.

The viscosity of ice cream mixes is shown in Figure 1.

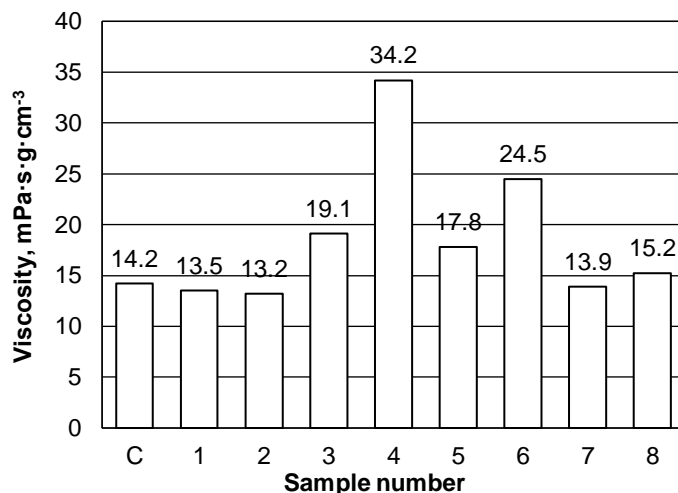


Figure 1. Viscosity of ice cream mixes with structuring ingredients.

Samples:

- | | |
|---|--|
| (C) control – mix of classic composition with Vianoks C45 stabilization system; | 5 – mix with β -glucan from oats and unfermented vegetable purée; |
| 1 – mix with β -glucan from oats; | 6 – mix with β -glucan from oats and fermented vegetable purée; |
| 2 – mix with β -glucan from yeast; | 7 – mix with β -glucan from yeast and unfermented vegetable purée; |
| 3 – mix with Vianoks C45 stabilization system and unfermented vegetable purée; | 8 – mix with β -glucan from yeast and fermented vegetable purée. |
| 4 – mix with Vianoks C45 stabilization system and fermented vegetable purée; | |

The viscosity of the control sample (C) was taken as a reference for conducting a comparative analysis of the effectiveness of the structuring ability of β -glucans from oat and yeast, both individually and in combination with pectin-containing vegetable purées. It was established that the structuring ability of β -glucans is quite high, but somewhat lower, compared to the stabilization system. β -glucan from oat in all combinations structures was more effective than β -glucan from yeast. This applies both to mixes with β -glucans and in the case of their combination with vegetable purées, which is explained by the different molecular structure and physicochemical properties of these polysaccharides. Thus, the chemical structure of β -glucan from oat is an unbranched polysaccharide formed from glucopyranose residues connected by β -(1-4) bonds and isolated β -(1-3) bonds. Oat β -glucan has a very high solubility in water (Synytsya et al., 2014). The chemical structure of β -glucan from the yeast *Saccharomyces cerevisiae* is represented by a complex of linear β -(1-3) chains with residual straight chains connected to them by long branches connected through β -(1-6) bonds (Aboushanab et al., 2019; Suzuki, et al., 2021). Therefore, it can be assumed that the high solubility and mobility of linear macromolecules of oat β -glucan in an aqueous environment with the formation of numerous low-energy bonds provide more effective structuring of ice cream mixes compared to β -glucan from yeast.

In the presence of vegetable purées in all samples, the viscosity significantly increases, which is explained by the probable interaction between macromolecules of β -glucans and pectin with the formation of complex three-dimensional structures. It should be noted that the greatest manifestation of such interaction was in case of combination of the Vianoks C45

stabilization system with pectin-containing purées. A greater manifestation of this effect is characteristic of fermented purée with an increased content of soluble pectin, which is quite understandable. The same pattern is observed for samples with vegetable purées that contain β -glucans.

Figure 2 and 3 show viscoelastic behavior of the test samples. The control sample with the stabilizing structuring system Vianoks C45 (mono- and diglycerides of fatty acids, guar gum, locust bean gum and carrageenan) is a weak gel (Figure 2, 3). The complex viscosity of the sample decreases with an increase in the frequency, and then increases (U-shaped), which is associated with a decrease in the tangent of the phase angle with an increase in frequency. The share of elastic properties in relation to viscous properties is increasing (Tomczyńska-Mleko et al., 2016). Probably the presence of several compounds with long molecular chains causes increased friction between them and corresponding contacts at higher frequencies. At very low frequency, the dispersion behaves as a predominantly viscous material (phase angle tangent greater than 1). However, when the frequency increases, the material increases its elastic properties (the tangent of the phase angle decreases) due to the interaction between macromolecules and their entanglement (Zhang, 2010). Shah et al. (2020) found that complex viscosity decreased with increasing frequency, but at higher frequency, complex viscosity increased. At a lower frequency, the dispersion behaves as a pseudo-plastic material, but at a higher frequency, a rheopectic behavior is observed.

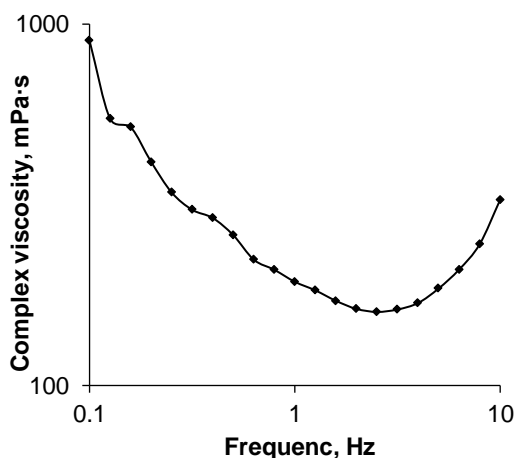


Figure 2. Complex viscosity of the control sample at variable frequency

For sample No1 with oat β -glucan, a characteristic intersection of the G' and G'' graphs is observed (Figure 4), which indicates even greater entanglement of the chains. Agbenorhevi et al. (2011) found that the mechanical spectra of the investigated oat β -glucan isolates were typical of solutions of entangled biopolymers. Atomic force microscopy images showed the formation of β -glucan aggregates connected by individual polymer chains, heterogeneously scattered throughout the dispersion. Sample No 2 with yeast β -glucan behaved similarly.

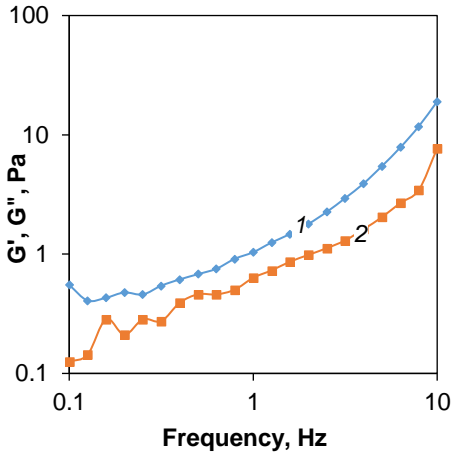


Figure 3. Ratio of the shear modulus (elastic component) to the shear modulus (viscous component) of the control sample at variable frequency

- 1 – Shear modulus (elastic component), Pa;
- 2 – Shear modulus (viscous component), Pa

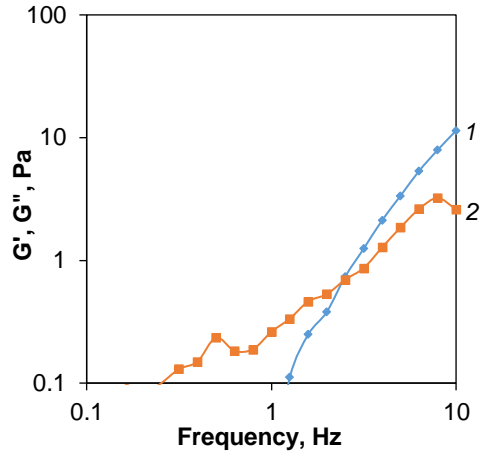


Figure 4. Ratio of shear modulus (elastic component) to shear modulus (viscous component) of sample No 1 at variable frequency

Samples No3 and No4 are elastic materials, the viscosity of which decreases with frequency (Figure 5 and 6). The viscosity of this dispersion exceeds the viscosity of previous preparations, which is probably due to the addition of beet puree.

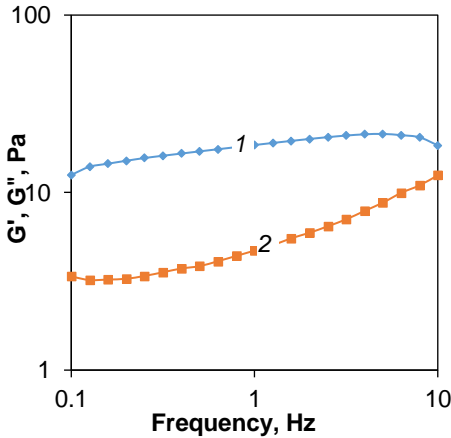


Figure 5. Ratio of the shear modulus (elastic component) to the shear modulus (viscous component) of sample No 3 at variable frequency

- 1 – Shear modulus (elastic component), Pa;
- 2 – Shear modulus (viscous component), Pa

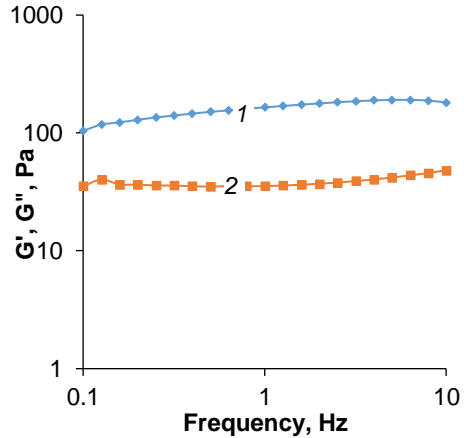


Figure 6. Ratio of the shear modulus (elastic component) to the shear modulus (viscous component) of sample No 4 at variable frequency

Sample No 5 shows very interesting rheological properties (Figure 7). At lower frequencies, the sample is elastic. After exceeding a certain value of the frequency, the structure collapses, and the value of the shear modulus (elastic component) suddenly drops. The module values overlap, and the sample is more viscous than elastic. This is confirmed by the increasing values of the tangent of the phase angle. The detected effect is positive from a technological point of view, because during freezing of ice cream mixes, they are saturated with air, followed by a uniform redistribution of air bubbles throughout the entire volume of the product. This process is effective under the condition of reducing the degree of structuring of mixtures during intensive mechanical processing. Similar behavior is demonstrated by sample No 6.

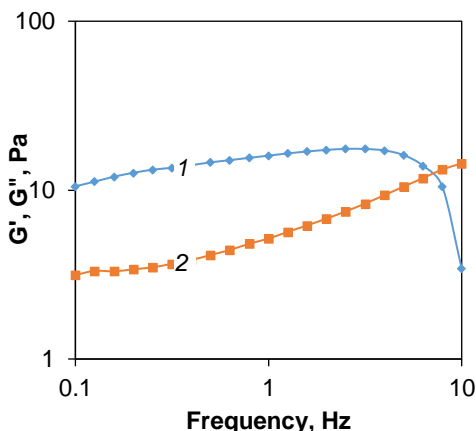


Figure 7. The ratio of the shear modulus (elastic component) to the shear modulus (viscous component) of sample No 5 at variable frequency:

- 1 – Shear modulus (elastic component), Pa;
- 2 – Shear modulus (viscous component), Pa

In use of different β -glucan from yeast with fermented and unfermented vegetable purée (samples No 7 and No 8), the structure of the samples did not deteriorate as a whole with increasing frequency.

The diagram in Figure 8 represents the correlation between storage modulus values reported at 10 Hz and ultrasonic viscosity. There is a strong linear correlation between these rheological properties ($R^2 = 0.82$). In previous studies, Tomczyńska-Mleko et al. (2022) found a linear correlation between complex modulus and ultrasonic viscosity ($R^2 = 0.91$), complex modulus and hardness ($R^2 = 0.89$), and ultrasonic viscosity and hardness ($R^2 = 0.82$). The highest correlation was found between the complex modulus and ultrasonic viscosity. The highest value of a correlation between complex modulus and ultrasonic viscosity was probably caused by the fact, that both methods used small strain measurements (Tomczyńska-Mleko et al., 2022).

At the next stage, to study the influence of structuring ingredients of different origin on the state of the aqueous phase of ice cream mixes, the water activity and surface tension of the control and experimental samples were determined (Table 1).

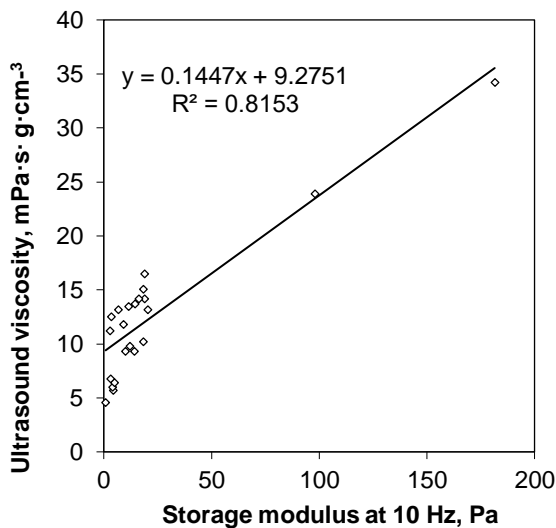


Figure 8. Correlation between ultrasonic viscosity and viscoelastic modulus at 10 Hz

Table 1
Water activity and surface tension of ice cream mixes with different structuring ingredients
($P \geq 0.95$; $n=3$)

| Sample numbers of mixtures with structuring ingredients | Water activity, a_w | Surface tension, mN/m |
|--|-----------------------|-----------------------|
| Control (Vianoks C45) | 0.04±0.041 | 44.088±1.990 |
| No1 (oat β -glucan) | 0.947±0.042 | 46.621±1.444 |
| No 2 (yeast β -glucan) | 0.959±0.040 | 49.696±1.551 |
| No 3 (Vianoks C45+non-fermented vegetable puree) | 0.923±0.041 | 43.293±1.118 |
| No 4 (Vianoks C45+fermented vegetable puree) | 0.855±0.044 | 41.428±1.122 |
| No 5 (oat β -glucan + non-fermented vegetable puree) | 0.933±0.043 | 45.893±1.118 |
| No 6 (oat β -glucan + fermented vegetable puree) | 0.893±0.043 | 43.827±0.903 |
| No 7 (yeast β -glucan + unfermented vegetable puree) | 0.948±0.040 | 46.428±0.990 |
| No 8 (yeast β -glucan + fermented vegetable puree) | 0.940±0.043 | 43.928±1.505 |

According to the data given in Table 1, the correlation between the values of water activity and surface tension is traced. The lowest water activity and surface tension are observed for sample No 4 (combination of hydrocolloids and surface-active compounds of the Vianoks C45 stabilization system and soluble pectin in fermented vegetable purée). Among the samples that contain only natural structuring ingredients the closest to the control is sample No 6, in which the " β -glucan oat + fermented beetroot purée" complex exerts the most significant influence on the aqueous phase. This sample is an alternative substitute for the control sample, which contains mono- and diglycerides of fatty acids and high-value polysaccharides as part of the Vianoks C45 stabilization system. It should also be noted that the fermented vegetable purée itself has a rather significant effect on the specified physical characteristics of ice cream mixes in all its combinations with other structuring ingredients.

This is explained by the content in fermented vegetable purée of at least 1.0% of soluble pectin (Sapiga et al., 2021), which ensures its additional presence in mixtures in the amount of at least 0.15%.

It should also be noted that the structuring ability of the mix samples correlates to some extent with water activity, in particular, the maximally structured samples No 4 and No 6 showed the lowest water activity (0.855 and 0.893, respectively). The same effect was observed by Mazurkiewicz and Tomasiak (2001) in solutions of sugar, salt, and glycerin, which allows controlling the activity of water in solutions with the required viscosity and vice versa.

Since viscosity and surface tension are determined by intermolecular bonds, we expected a positive correlation between these physical characteristics and found it in all samples. However, using the example of aqueous solutions of agar polysaccharides and starch-containing flour, Wei et al. (2014) found that with an increase in the viscosity of aqueous solutions, the surface tension was either the same as water or slightly lower. The authors explained this effect by assuming that internal friction, caused by the interaction between macromolecules of polysaccharides with numerous polar groups, affects viscosity more than surface tension. In our case, all samples were multicomponent mixes containing low-molecular water-soluble compounds (sucrose, lactose, salts) and high-molecular compounds (milk proteins, polysaccharides), and the control sample and samples No 3 and No 4 were emulsifiers (mono-, diglycerides of fatty acids), therefore the surface tension of the mixes was significantly different from that of water and correlated with the viscosity and activity of water.

Thus, based on the set of research results, it can be stated that the most promising for use in the composition of low-fat ice cream with natural ingredients is oat β -glucan in combination with fermented beetroot purée in the specified quantities of 0.5% and 15%, respectively.

Conclusions

1. Fermented beet purée containing at least 1.0% soluble pectin has the greatest impact on the structural and mechanical characteristics of low-fat ice cream mixes in all its combinations with other structuring ingredients. In turn, oat β -glucan shows greater technological activity compared to β -glucan from yeast, including when combined with soluble pectin of vegetable purée. Mixes of ice cream with oat β -glucan and vegetable purée at lower frequencies of measuring viscoelastic properties show elasticity, but after exceeding a certain frequency value, the structure is destroyed and the mixes show greater viscosity than elasticity.
2. The correlation between viscosity, water activity and surface tension of low-fat ice cream mixes was revealed, which is explained by the presence of a complex of low-molecular (sucrose, lactose, salts) and high-molecular compounds (proteins, polysaccharides) in multicomponent mixtures.
3. An alternative substitute for the Vianoks C45 stabilization system (mono- and diglycerides of fatty acids + polysaccharide complex) in the amount of 0.5% is a complex of natural ingredients - oat β -glucan and fermented beet pulp in amounts of 0.5 and 15%, respectively.
4. The perspective of further research is to optimize the ratio between structuring natural ingredients (oat β -glucan and fermented vegetable purée) to achieve appropriate values of ice cream quality indicators (overrun, resistance to melting, distribution of dispersed particles), including during storage.

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Resource- and energy-saving methods of joint use of by-products and intermediates in alcohol production

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Abstract

Keywords:

Ethanol
Rectification
Plates
Column
Impurities
Fusel

Introduction. The aim of the work was to study and substantiate the effectiveness of energy-saving methods for the joint processing of alcohol-containing fractions in a cyclic action column, to increase the degree of alcohol purification from volatile impurities.

Materials and methods. The study was carried out in a typical impurity concentration column and an experimental cyclic action column. The liquid flow rate was monitored using constant differential pressure flowmeters, the concentration of ethyl alcohol and volatile impurities was determined by areometric and chromatographic methods, the degree of impurity emission and the multiplicity of their concentrating were determined by the calculation method.

Results and discussion. The application of the methods proposed makes it possible to carry out joint use of by-products and intermediate products of alcohol production (head and fusel fractions) in a cyclic action rectification column equipped with scaly plates with a variable free cross-section. This allows to obtain high-quality rectified alcohol, to increase its yield by 3.8–4.0% from one tonne of notional starch or by 10.8% compared to the known method and to reduce specific vapor consumption by 40% (from 20 to 12 kg/dal of anhydrous alcohol introduced to the feed plate). Extending the contact time of steam and liquid on the column plates to 40 sec allows for complete emission of esters, increasing the degree of aldehyde recovery by 25% and the higher alcohols of fusel oil and methanol by 40%. The proposed technical solutions and selected technological modes make it possible to increase the efficiency of separation of the alcohol-containing mixture in the decanter, increase the multiplicity of concentrating of aldehydes and esters by 26%, higher fusel oil alcohols by 40%, methanol by 37%, reduce the loss of ethyl alcohol with the impurity concentrate, the amount of alcohol-containing waste, the metal consumption of technological equipment and the cost of rectified alcohol.

Conclusion. The proposed methods allow the maximum purification of ethyl alcohol from head and intermediate impurities in a cyclic action rectification column, to obtain high-quality rectified alcohol, to reduce energy consumption and loss of alcohol with waste.

Article history:

Received 20.05.2022
Received in revised
form 17.10.2022
Accepted 1.12.2022

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DOI: 10.24263/2304-
974X-2022-11-3-4

Introduction

The rise of energy prices is the reason for the development and implementation of energy-saving ways to increase the yield of rectified ethyl alcohol by processing alcohol-containing by-products. Intermediates products include vapor condensates from the condenser of the beer and rectification columns, from the carbon dioxide separator condenser and alcohol traps, fusel alcohol, fusel rinse water and unpasteurized alcohol.

It is known that the yield of rectified ethanol in typical distillation equipment is 93–95% of the amount of alcohol introduced with the beer. Part of the alcohol (0.8–1.2%) is lost with waste (stillage, luther water and non-condensable gases). With the head fraction and fusel alcohol, 3–5% of ethyl alcohol is emitted from the unit, with fusel oil 0.3–0.45% of the alcohol. The anhydrous part of the head fraction contains 92–97% ethyl alcohol and 3–8% volatile impurities. The inclusion of a impurity concentration column (ICC) in the technological scheme allows to increase the yield of rectified ethyl alcohol from 94–96 to 98–98.5% and to emitted volatile impurities from the unit in concentrated form (Shiyan et al., 2009). The composition of fusel alcohol contains 25–30% water, 45–60% ethanol, 5–20% higher alcohols C₃–C₅ (mainly propanol and isobutanol), 0.3–0.8% esters, small amounts of volatile nitrogenous substances, aldehydes and acids. The fusel alcohol is taken from the 18th, 20th, 22nd, and 24th plates of the rectification column in the amount of 0.8–2.5%, and the fusel fraction from the 5th, 7th, 9th, and 11th plates of the column in the amount of 3–5% of the amount of alcohol introduced to the feed plate. Its ethanol content is 5–40%. For ethanol extraction, fusel alcohol, together with the fusel fraction, is fed to a fusel column (Mendoza-Pedroza et al., 2021).

The inclusion of additional columns in the scheme of the distillation equipment requires increased energy consumption, increased metal consumption of equipment, which leads to a decrease in the cost of rectified alcohol (Biasi et al., 2020). Thus, the use of ICC requires an increase in the consumption of heating vapor to 20 kg/dal in terms of anhydrous alcohol (a.a) introduced into the column, and hot softened water for hydroselction in the amount of 11.7–20.5 kg/kg a.a, depending on the type of raw material.

The efficiency of the ICC is determined by the degree of distillation residue from volatile impurities formed at all technological stages of production. Theoretical developments prove that the degree of separation of organic impurities and ethyl alcohol depends on the difference in their evaporation coefficients. For the head and intermediate impurities, this difference reaches its maximum value at low alcohol concentrations in the solutions, and for the final impurities – at high ethanol concentrations. Effective emitted of head impurities (esters and aldehydes) occurs under conditions of deep hydroselction at a concentration of ethyl alcohol at the bottom of the column of 6–8% vol. To emitted intermediate impurities (higher alcohols of fusel oil), the concentration of ethyl alcohol must be reduced to 4–5% vol. To increase the coefficient of rectification of final impurities of low boiling point impurities (methyl alcohol) it is advisable to perform moderate hydroselction to ensure the concentration of ethanol on the plates within 60% mol. along the entire height of the column.

From practical experience, it is known that for the joint processing of head and fusel fraction in a typical ICC, to increase the number of contact devices to 51–57, and to increase the consumption of heating steam by 28.7% (from 2.56 to 3.59 kg/kg a.a) (Kiss et al., 2014). Despite this, the known processing methods do not ensure effective extraction of the head and upper intermediate impurities, which negatively affects the quality of rectified alcohol.

The efficiency of purification of ethyl alcohol, which is part of by-products and semi-products products, depends not only on the degree of extraction and multiplicity of concentrating volatile impurities, but also on the organization of their selection from the places

of their maximum accumulation. In order to increase the efficiency of this process, the deflemmator of ICC is connect with a decantator (Kiss, 2015).

In the decanter the condensate of vapour (phlegm) from the dephlegmator is separated into upper and lower layers. The upper layer concentrates water insoluble impurities, which are removed from the unit. The purified aqueous-alcoholic liquid from the bottom of the decanter is fed on the top plate of the column. In case of poor separation of the impurities can enter the column acetic, formic, crotonic aldehydes, some fusel oil alcohols (n-propyl and isopropyl alcohols), acrolein – impurities that significantly impair the quality of rectified ethyl alcohol. The most of these impurities enter the liquid at the bottom of the column and further into the beer. Increasing their concentration in the beer leads to increased consumption of heating steam in the beer column. The known processing methods do not provide effective demulsification of higher alcohols of fusel fractions due to the temperature in the decanter being much higher than 25–35 °C. Under such conditions, higher alcohols, which are concentrated in the upper layer of the decanter, retain more water and ethanol, resulting in a decrease in the yield of rectified ethanol (Mendoza-Pedroza et al., 2015).

The use of cyclic rectification technology is a relatively new approach to solving the problem of energy saving and increasing the degree of alcohol impurities. A significant number of scientific works by famous scientists are devoted to research in this area, but the known processing methods have not found wide practical application (Andersen et al., 2018; Kiss, 2014; Bastian et al., 2012; Nielsen et al., 2017; Toftegard et al., 2016; Rasmussen et al., 2020).

To solve the actual problem, the authors proposed resource- and energy-saving methods for the extraction of ethyl alcohol from alcohol-containing by-products and semi-products of alcohol production and its effective purification from impurities in the mode of controlled rectification cycles (Maleta et al., 2015, Buliy et al., 2019). To implement them, was developed a design of a ICC (patent UA 124733. Column mass-exchange apparatus of cyclic action) and an equipment and technological scheme for its inclusion in operation.

The adopted technical solutions made it possible to eliminate the disadvantages inherent in the known method, to process fractions enriched with head, intermediate and terminal impurities in one column, to improve the quality of rectified ethyl alcohol by achieving a state of contacting phases (vapor and liquid) close to equilibrium on its plates, to maximize the removal of volatile impurities, and to reduce the specific consumption of heating steam for the processing process (Bulii et al., 2021).

The aim of the work was to research and justify of the efficiency of energy-saving methods of joint processing of by-products and intermediates of alcohol production in the ICC of cyclic action: selection of optimal technological modes of operation, at which the degree of extraction and multiplicity of concentrating of head, intermediate and terminal impurities of alcohol will be maximized; determination of the specific consumption of heating steam in the experimental column.

Research tasks:

- To establish the optimal technological parameters of ICC operation for efficient joint processing of fractions enriched with head, intermediate and terminal impurities;
- To determine the degree of extraction and the multiplicity of concentrating of organic volatile impurities of alcohol in a typical column operating in a stationary mode and a cyclic action experimental column;
- To investigate and select the optimal technological modes for effective phlegm stratification in the decanter, increase of multiplicity concentrating impurities, degree of purification of phlegm and distillation residur in the experimental column;
- Determine the specific consumption of heating steam in the experimental column of cyclic action.

Materials and methods

Research objects

1. Experimental column of cyclic action for impurity concentrating (ICC). The experimental column was made of AISI 304 stainless steel and equipped with scale plates (Figure 1).



Figure 1. General view of an impurity concentration column

Technical characteristics of the column: diameter – 950 mm; number of plates –30; distance between plates – 300 mm; free cross-section of the plate during the period of liquid staying on its surface – 2.5%, during the period of liquid overflow – 51.5%.

The absence of overflow and receiving devices made it possible to increase the surface of phase contact on each plate by 15% and the coaxial arrangement of the scales to increase the efficiency of mass- exchange and eliminated the possibility of liquid droplets being carried to the upper plates. All the plates contained movable sections connected to pneumatic cylinders and modern computer-integrated means (patent UA 136561. Mass-exchange contact plate).

The operation of a cyclic mass-exchange plate is shown schematically in Figure 2.

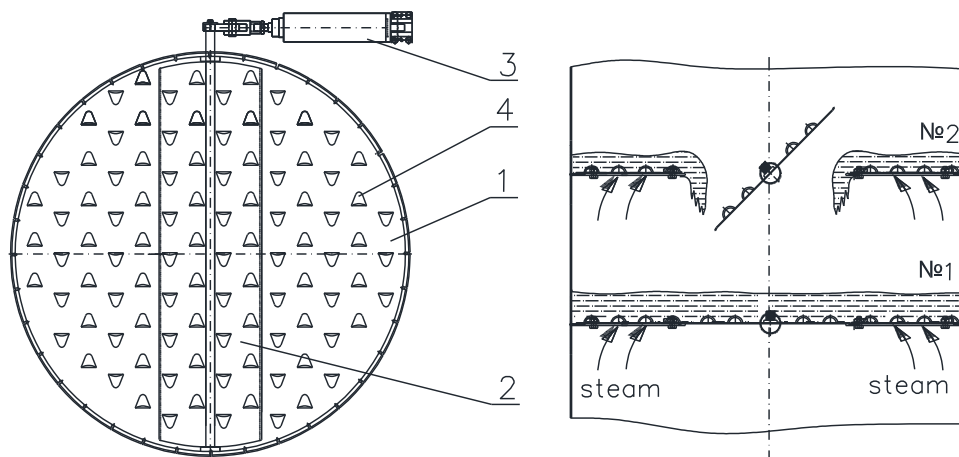


Figure 2. Cyclic mass-exchange plate with a variable free cross-section

1 – plate web; 2 – movable segment; 3 – drive mechanism; 4 – scales

The column was operated by continuously supplying heating steam to its lower part and liquid to the upper plate and periodically overflowing liquid from plate to plate from top to bottom after a set time of its delay on each plate. The ratio of the cross-sectional area of the overflow hole to the cross-sectional area of the plate at the time of overflow of (0.5:1) ensured an instantaneous decrease in the velocity of vapor in the holes of the scales to 1.5–1 m/s, as a result of which the liquid spilled through all the holes. Thus, the cycles of mass-exchange and overflow occurred alternately according to a given algorithm of pneumatic cylinders (patent UA 123917. Method of mass-exchange between liquid and vapor in a column apparatus).

After the rotation of the movable segment 2, the liquid overflowed onto the web 1 of the plate 1 from the plate 2 above it through the hole that had formed. During this period, the movable segment 2 of the web 1 of the plate №1 was closed. The heating steam entered through the slits of the scales 4 and came into contact with the liquid on the plate 1. During the period of mass-exchange, the steam velocity in the slits of the scales 4 was maintained within 12–14 m/s, so the liquid was kept on the plate. After the set time of the liquid staying on the plate № 1, due to the action of the pneumatic cylinder 3, its movable segment 2 was turned, and the liquid instantly overflowed to the plate below through the hole formed.

2. The unit for ethyl alcohol extraction from alcohol-containing fractions. The processing of alcohol-containing fractions enriched with head, intermediate and terminal impurities was carried out in three ways. The hardware and technological scheme of the unit for the implementation of method I is shown in Figure 3 (patent UA 137550. Method for the joint distillation of alcohol-containing fractions enriched with head, intermediate and terminal impurities).

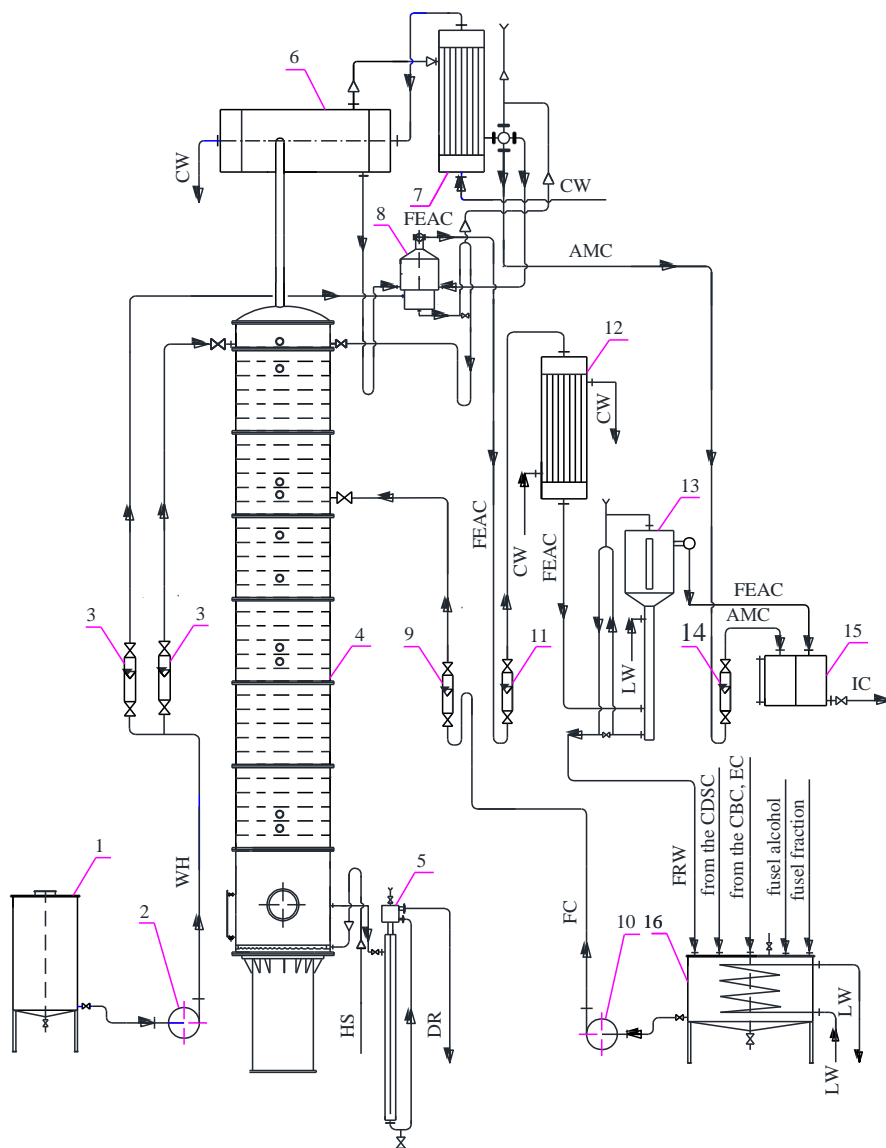


Figure 3. Installation for joint processing of head and fusel fractions by method I:

1 – water container; 2,10 – centrifugal pumps; 3,9,11,14 – flowmeters; 4 – impurity concentration column (ICC); 5 – hydraulic shutter; 6 – dephlegmator; 7 – condenser; 8 – decanter; 12 – cooler; 13 – extractor; 15 – impurity concentrate container; 16 – alcohol-containing fractions container.

Notation conventions:

CW – cooling water; HS – heating steam; DR – distillation residue; WH – water for hydroselection; FRW - fusel rinse water; FC – feed of column; FEAC – fusel and ester-aldehyde concentrate; AMC – aldehyde and methanol concentrate; LW – luther water; BC – beer column; EC – ether column; CBC – condenser of beer column; CDSC – carbon dioxide separator condenser; IC – impurity concentrate.

The equipment and technological scheme of the unit for processing by-products and intermediates of alcohol production according to method II is shown in Figure 4 (patent UA 137553. Method of joint processing of head and fusel fractions).

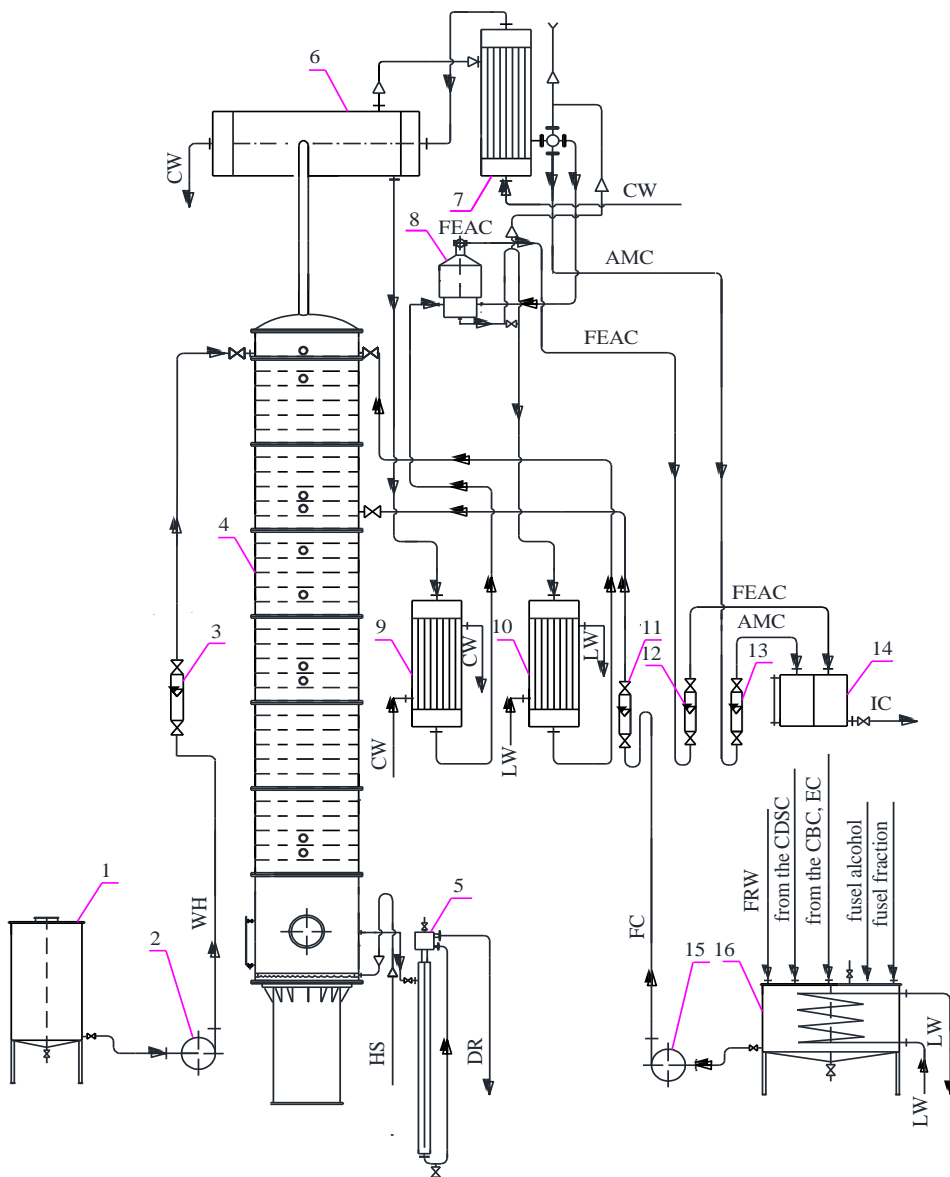


Figure 4. Unit for joint processing of head and fusel fractions by method II:

- 1 – water container; 2,15 – centrifugal pumps; 3,11,12,13 – flowmeters;
- 4 – impurity concentration column (ICC); 5 – hydraulic shutter; 6 – dephlegmator;
- 7 – condenser; 8 – decanter; 9 – cooler; 10 – heater; 14 – impurity concentrate container; 16 – alcohol-containing fractions container.

The equipment and technological scheme of the unit for processing by-products and intermediates of alcohol production according to method III is shown in Figure 5 (patent UA 137555. Method of ethyl alcohol extraction from head and fusel fractions).

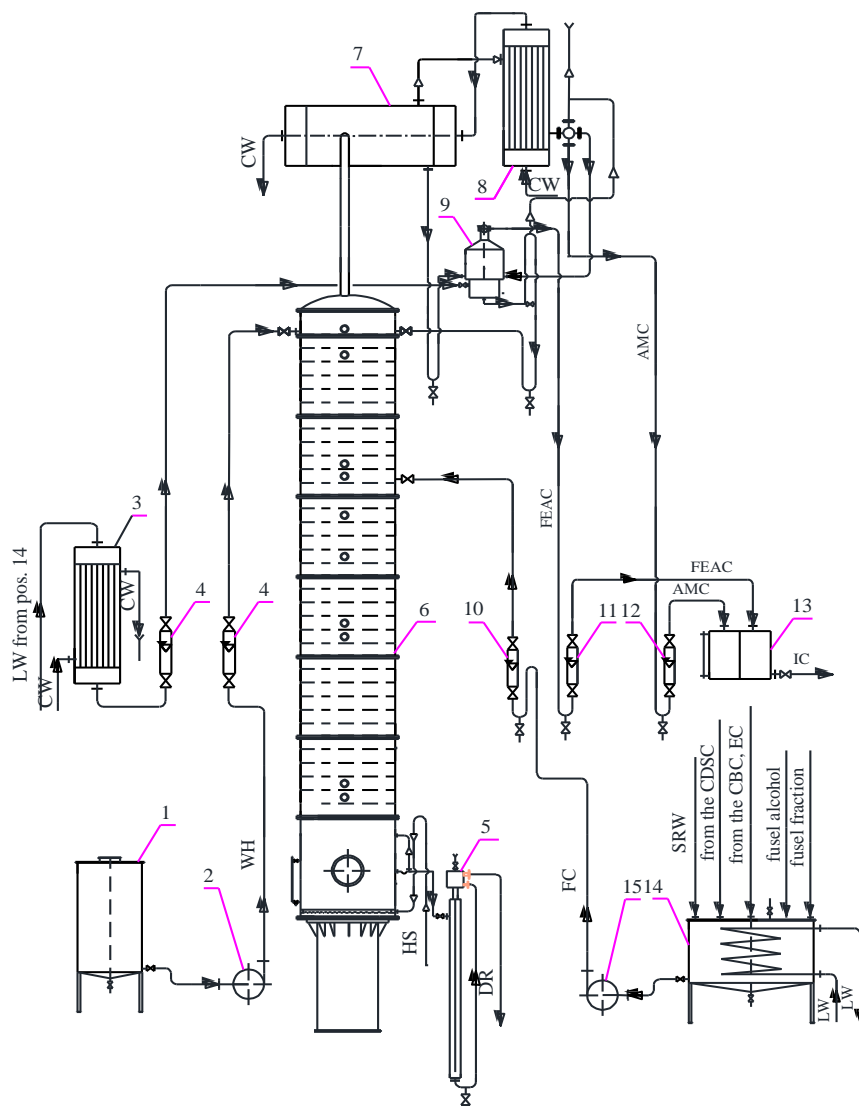


Figure 5. Unit for joint processing of head and fusel fractions by method III

- 1 – water container; 2,15 – centrifugal pumps; 3 – cooler; 4,10,11,12 – flowmeters;
- 5 – hydraulic shutter; 6 – impurity concentration column; 7 – dephlegmator;
- 8 – condenser; 9 – decanter; 13 – impurity concentrate container;
- 14 – alcohol-containing fraction container.

Research methods

Analytical, chemical, physico-chemical and computational methods were used to evaluate the results obtained, using instruments and research methods used in the production of rectified ethyl alcohol.

Liquid consumption. The consumption of alcohol-containing fractions, water for hydroselction, distillation residue from the impurity concentration column and rectified alcohol was monitored using flowmeters (Polulyah et al., 2012).

The principle of their operation is based on the perception of the dynamic head of the controlled medium, which depends on the flow rate, by a sensing element (float) placed in the flow. As a result of the flow, the sensing element moves along the height of the flowmeter, and the amount of movement serves as a measure of flow. The readings were taken on the scale of the flowmeter, graduated by water in dm³/h.

Concentration of ethyl alcohol in water-alcohol solutions. The concentration of ethyl alcohol in the aqueous-alcoholic liquids was determined by the areometric method (Yanchevskiy et al., 2002). The test solution was poured into a 250 cm³ glass cylinder, the temperature was measured with a thermometer with a division price of 0.1 °C, and then the ASP-1 alcoholmeter was immersed. The actual concentration of ethyl alcohol at a temperature of 20 °C was determined from the readings of the alcoholmeter and using special tables to make appropriate corrections for temperature.

Concentration of volatile alcohol impurities. The concentration of volatile impurities in alcohol by-products and intermediates, the distillation residue of the impurity concentration column, the impurity concentrate and the rectified ethyl alcohol was determined on a gas chromatograph with an HP FFAP 50 m × 0.32 m column (Dewulf, 2002; Plutowska et al., 2008; Steven et al., 2002). The analysis of the experimental samples was carried out three times. The average values were chosen as determinative.

The grade of extraction and concentration ratio of volatile alcohol impurities. The degree of extraction (α) and multiplicity of concentration impurities (β) of key organic impurities of alcohol were calculated by the formulas:

$$\alpha = \frac{X_{fc}}{X_{dr}}, \quad \beta = \frac{X_{feac}}{X_{fc}}$$

where X_{fc} , X_{feac} , X_{dr} – the concentration of volatile impurities of alcohol on the feed plate of column, in the fusel ester-aldehyde concentrate and the distillation residue of the impurity concentration column (ICC), mg/dm³ in terms of a.a., respectively (Shiyan et al., 2009).

Studied modes

Joint processing of by-products and intermediates was carried out in stationary and cyclic modes of work of the impurity concentration column (in the existing typical and experimental column), which alternately operated as part of an indirect-acting distillation unit (Bulii et al., 2021; Mischenko et al., 2020). The movement of volatile alcohol impurities in the columns of the distillation plant is shown schematically in Figure 6.

The plate of feed of the impurity concentration column was supplied with the head fraction of ethyl alcohol, fusel fraction and fusel alcohol from the rectification column, fusel rinse water, fractions from the condenser of the beer column and the condenser of the carbon dioxide separator. The total amount of alcohol containing fractions was 700 dm³/h (250 dm³/h in terms of a.a). The concentration of ethyl alcohol in them was 35.7% vol. Hot luther

water in the amount of 3500–4100 m³/h was continuously supplied to the upper plate of column for the hydroselection of alcohol impurities. The temperature of the luther water was 90–92 °C. In steady-state mode, the liquid was poured from plate to plate from top to bottom continuously, while in cyclic mode, it was poured periodically after a set delay time on each plate.

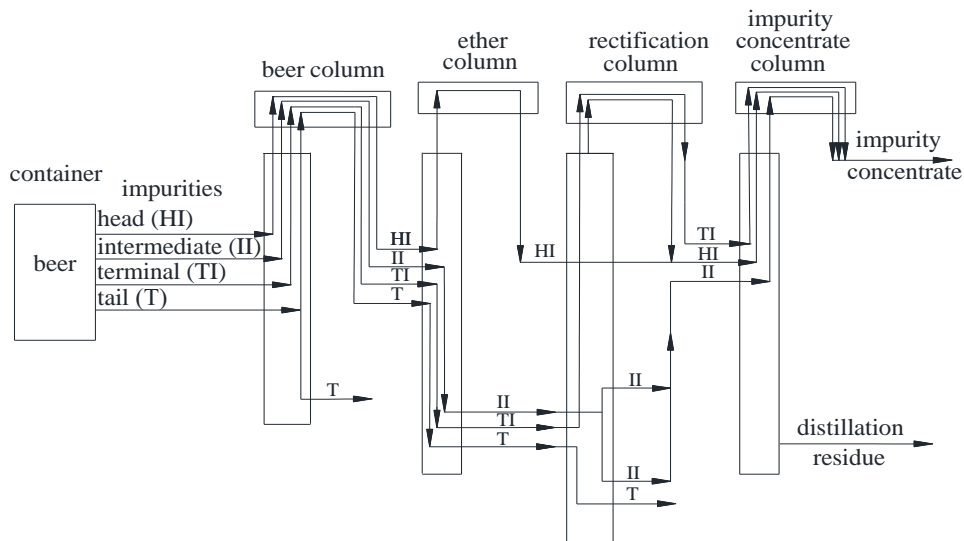


Figure 6. The movement of volatile alcohol impurities in the columns of the distillation plant of indirect action

HI – head impurities; II – intermediate impurities; TI – terminal impurities;
T – tail impurities

The fluid retention time was 40 s, and the time for its overflow from the upper plate to the lower plate was 1.7 s. The height of the liquid layer on the plates was 35–40 mm. The pressure in the lower part of the column was maintained within 120 kPa, and in the upper part 0.3 kPa. The temperature at the bottom of the column was 101 °C, and above the top plate 94 °C. The concentration of ethyl alcohol of the distillation residue at the bottom of the column was regulated by the flow rate of luther water and maintained within 3.8% vol.

In the experimental impurity concentration column, the vapor velocity in the holes of the scales during the period of liquid retention on the plates was 12–14 m/s, and during the period of its overflow 1.5–1 m/s (Bulii et al., 2021; Krivchun et al., 1986). The change in the vapor velocity occurred by changing the free cross-section of the plate at the time of opening and closing the overflow hole. The liquid throughput of the experimental column was 5000 dm³/h. The phlegm from the deflagmator was sent to the decanter, where the liquid was stratified at an optimum temperature of 20–40 °C (Bulii et al., 2022). The water-alcohol liquid freed from most of the impurities from the lower part of the decanter in the form of phlegm was sent to the upper plate of the column for its irrigation. From the upper part of the decanter, SEAC was taken in the amount of 0.4–0.6% of the amount of rectified alcohol. AMC was taken from the condenser acceleration column in a ratio of (1:2) to FEAC in the amount of 0.2–0.3%

Stages of research

At the first stage, we studied the efficiency of joint processing of alcohol-containing by-products and intermediates using a well-known method with the separation of all concentrated alcohol impurities in the form of one product – SEAC in an experimental column operating in a stationary mode (Patent UA 69511. Rectification unit for the extraction of ethyl alcohol from fractions enriched with organic impurities).

During the rectification process, the alcohol-containing mixture was divided into two streams: the upper one, which contained head and intermediate alcohol impurities, and the lower one, which contained the water-alcohol mixture freed from them. The vapors coming out of the upper part of the column were fed first to the deflagrator and then to the condenser. Most of the vapors condensed in the deflagrator (high-boiling components – water, higher alcohols, esters and ethanol), while low-boiling components – aldehydes, esters, a small amount of higher alcohols and methyl alcohol condensed in the condenser.

The phlegm from the deflagrator was fed to the top plate of the column for its irrigation, and the condensate from the condenser flowed by gravity to the decanter. In the decanter, the heterogeneous mixture was stratified to form an upper layer – fusel and ester-aldehyde concentrate (FEAC), which included esters, aldehydes, esters, fusel oil alcohols, and a lower layer – an aqueous-alcoholic liquid free of head, part of intermediate and terminal impurities. The FEAC was removed from the unit into a separate container, and the water-alcohol liquid was fed to the upper plate of the column for its irrigation. The yield of FEAC was 0.4–0.6% of the amount of rectified alcohol. The aqueous-alcoholic liquid from the bottom of the impurity concentration column, was pump into the beer.

At the second stage, we studied the efficiency of processing alcohol-containing fractions using Method I (Figure 3).

The fractions enriched with head (esters and aldehydes), intermediate (higher alcohols of fusel oil), and terminal (methyl alcohol) impurities were fed to the alcohol-containing fraction tank 16, where they were heated by the heat of hot luther water to a temperature of 78–80 °C. Then they were fed to the feed plate of column 4 by a centrifugal pump 10. In the process of extractive rectification, the alcohol-containing mixture was separated into two streams: the upper one, which contained the head, intermediate and terminal alcohol impurities, and the lower one, which contained the water-alcohol liquid freed from them. The vapors from the upper part of the column were fed first to the dephlegmator 6 and then to the condenser 7. In its lantern, the mixture was stratified: water-insoluble aldehydes, esters, and higher alcohols were concentrated in the upper layer, and water-soluble aldehydes and methanol were concentrated in the lower layer, which were taken from the condenser to the container 15 in the form of aldehyde and methanol concentrate (AMC). The vapor condensate from the dephlegmator 6 with a temperature of 65 °C and the upper layer of liquid from the condenser lantern 7 flowed by gravity into the middle part of the decanter 8. To reduce the concentration of ethyl alcohol in the mixture from 65–68 to 30–40% vol., the calculated amount of hot luther water was supplied from the container 1 to the lower part of the decanter 8 by the centrifugal pump 2 through the flowmeter 3. The mixture was separated into an upper and a lower layer in the decanter. From the upper part of the decanter, FEAC was taken through the flowmeter 11, which was cooled in the cooler 12 to a temperature of 20–35 °C and sent to the lower part of the extractor 13. In the extractor, the FEAC was washed with luther water, which had a temperature of 20–35 °C and pH 5.0–5.5, to extract ethyl alcohol. The FEAC freed from alcohol was sent to container 15, and the fusel rinse water containing 12–15% vol. of ethyl alcohol was returned to container 16. The distillation residue from the

bottom of the impurity concentration column, free from volatile impurities, was fed to the upper zone of the concentration part of the ether column for hydroselction of impurities.

At the third stage, we studied the efficiency of processing alcohol-containing fractions using Method II (Figure 4). The method involved cooling the phlegm, which was taken from the dephlegmator 6, to a temperature of 20–35 °C in a cooler 9, separating the mixture in the decanter 8 into two layers – the upper (FEAC) and the lower (water-alcohol liquid purified from impurities), heating this liquid in the heat exchanger 10 with the heat of hot luther water, which had a temperature of 102–103 °C, to a temperature of 90–92 °C and supplying the hot liquid in the form of phlegm to the upper plate of the impurity concentration column for its irrigation.

At the fourth stage of the studies, joint processing of the alcohol-containing fractions were processed according to method III (Figure 5). To do this, hot luther water was first sent to the alcohol-containing fraction container 14 to heat the power supply, then it was cooled in the refrigerator 3 to a temperature of 10–15 °C and then fed to the lower part of the decanter 9. After mixing the cooled luther water with phlegm coming from the dephlegmator 7 in the decanter, the temperature of the mixture decreased from 65–68 to 20–35 °C, the concentration of ethyl alcohol in it decreased to 30–40% vol, and the pH was reduced to 5.0–5.5.

To determine optimal technological parameters of work of the column of cyclic action, in which the degree of extraction and multiplicity of concentrating of head, intermediate and terminal impurities of alcohol were the highest, a comparative analysis of efficiency of known and proposed by the authors methods of processing alcohol-containing fractions. In the course of research, samples were taken of fractions coming to the plate of feeding of the column (FC), the distillate residue (DR), impurity concentrate (IC), formed after mixing in the container of FEAC and AMC, rectified ethyl alcohol (REA) and carried out their analysis by chromatographic method. The results of the analysis of the test samples are presented in Table 1.

The calculated values of the degree of extraction (α) and the multiplicity of concentration (β) of volatile alcohol impurities under typical and cyclic rectification conditions are given in Table 2.

Results and discussion

Processing of by-products and intermediates by a known method in an impurity concentration column working in a stationary mode.

The use of a well-known method of processing alcohol-containing fractions made it possible to increase the yield of rectified ethyl alcohol by 3.5–3.7% from one ton of conditional starch and to remove volatile organic impurities from the unit in the form of a single product, which simplified the method of selection, storage and transportation of waste, but did not exclude the disadvantages listed below.

1. Table 1 shows that in the process of joint processing of the head and fusel fractions by the known method, the physical and chemical parameters of rectified ethyl alcohol did not meet the standard for the high-quality alcohol. The mass concentration of fusel oil, in terms of a mixture of isoamyl and isobutyl alcohols (1:1) in anhydrous alcohol, exceeded the standard by 10% (Pang et al., 2017).

Table 1

Concentration of volatile impurities in the feed, distillation residue, impurity concentrate and rectified ethyl alcohol

| Impurity name | Concentration, mg/dm ³ in terms of a.a. | | | | | | |
|-------------------|--|---------------------|--------|-------|--------------------|--------|--------|
| | FC | A well-known method | | | Methods I, II, III | | |
| | | DR | IC | REA | DR | IC | REA |
| Ethanol,% vol. | 30.5 | 3.8 | 75 | 96.3 | 3.8 | 67 | 96.3 |
| Aldehydes | 318.7 | 4.7 | 1689.1 | 1.2 | 2.8 | 2302.2 | 0.18 |
| - acetaldehyde | 242.3 | 4.7 | 1041.9 | 1.2 | 2.8 | 1396.7 | 0.18 |
| - methylacetate | 76.4 | traces | 672.3 | – | traces | 905.5 | – |
| Esters | 40.5 | 2.5 | 330630 | – | traces | 446615 | – |
| - ethylacetate | traces | 2.5 | traces | – | traces | traces | – |
| - isobutylacetate | 11.1 | traces | 2383.2 | – | traces | 3234.8 | – |
| - isoamylacetate | 29.4 | traces | 361.5 | – | traces | 494.4 | – |
| - ethylbutyrate | traces | traces | 327885 | – | traces | 442886 | – |
| Methanol,% | 0.18 | 0.007 | 1.7 | 0.005 | 0.004 | 2.7 | 0.0006 |
| Fusel oil | 105883 | 1180.4 | 434120 | 2.2 | 721.7 | 726464 | 0.88 |
| - isopropanol | 1.2 | 0.015 | 13.1 | 2.2 | traces | 22.4 | 0.88 |
| - n-propanol | 20002 | 1117.4 | 100.4 | – | 677.5 | 220.6 | – |
| - isobutanol | 20297 | 8.4 | 213118 | – | 4.9 | 357247 | – |
| - n-butanol | 362 | 4.4 | 579.2 | – | 2.7 | 1003.8 | – |
| - isoamylol | 65221 | 16.5 | 215230 | – | 13.8 | 367970 | – |

Notation conventions:

FC – feed of column; DR – distillation residue; IC – impurity concentrate;
REA – rectified ethyl alcohol.

Table 2

Calculated values of the grade of extraction (α) and concentration ratio (β) of volatile alcohol impurities

| Impurity name | A well-known method | | Methods I, II, III | |
|-------------------|---------------------|---------|--------------------|-------|
| | α | β | α | B |
| Aldehydes | 67.8 | 5.3 | 113.8 | 7.2 |
| - acetaldehyde | 51.6 | 4.3 | 86.5 | 5.8 |
| - methylacetate | max | 8.8 | max | 11.9 |
| Esters | 16.2 | 8163.7 | max | 11027 |
| - isobutylacetate | max | 214.7 | max | 291.4 |
| - isoamylacetate | max | 12.3 | max | 16.8 |
| Methanol | 25.7 | 9.4 | 45.0 | 14.9 |
| Fusel oil | 89.7 | 4.1 | 146.7 | 6.9 |
| - isopropanol | 80.0 | 10.9 | max | 18.7 |
| - n-propanol | 17.9 | 0.005 | 29.5 | 0.01 |
| - isobutanol | 2416.3 | 10.5 | 4142.2 | 17.6 |
| - n-butanol | 82.3 | 1.6 | 134.1 | 2.8 |
| - isoamylol | 3952.8 | 3.3 | 4726.2 | 5.6 |

2. An increase in the concentration of esters and higher alcohol of fusel oil in the distillate residue from the bottom of the column, and then in the beer, led to an increase in the consumption of heating steam for their extraction in the beer and ether columns. This is due to the fact that at high distillation temperatures of alcohol beer (95–105 °C), simultaneously with the release of volatile impurities, the interaction of alcohols, acids, aldehydes, amino acid breakdown products, sulfur compounds and other beer compounds occurred and a number of substances (aldehydes, esters, acetals of organic acids, etc.) were formed that deteriorate the quality of alcohol and reduce its yield. To ensure the efficient extraction of alcohol and related organic impurities from the beer, the beer column was operated with an excess of 5–10% steam at a steam excess coefficient of $\beta = 1.05\text{--}1.1$ (Bulii et al., 2022).

The continuous flow of distillation residue into the beer, which contained residues of intermediate and terminal impurities, led to their accumulation in the beer, an increase in the content of undesirable newly formed compounds in the beer distillate, the removal of which requires increased water consumption for their hydroselection in the ether column, and, accordingly, an increase in the consumption of heating steam (Simon et al., 2009).

3. In order to increase the degree of volatile impurities extraction and achieve the standard quality indicators of rectified ethyl alcohol a necessary condition was to increase the specific consumption of heating steam in the impurities concentration column to 20 kg/dal a.a. introduced to the feed plate. This is due to the fact that with the continuous overflow of liquid along the height of the column, the time of its stay on the plates and contact with steam was insufficient to create conditions close to the equilibrium state of the phases, under which the maximum extraction of impurities occurs. In addition, the method did not provide for cooling the phlegm to the temperature (25–30 °C) optimal for demulsification of higher fusel oil alcohols (Patil et al., 2002). At an elevated phlegm temperature (65–68 °C), the quality of the FEAC deteriorated: higher fusel oil alcohols, which were concentrated in the upper layer of the decanter, retained more water and ethanol, resulting in a decrease in the yield of rectified alcohol. Due to the high concentration of ethyl alcohol in the phlegm (65–70% vol.), enriched with head and intermediate impurities, the phlegm did not effectively separate in the decanter. As a result, water-soluble undesirable impurities (methyl alcohol, crotonic aldehyde, acrolein, isopropanol, etc.) from the bottom of the decanter together with the liquid first got to the upper plate of the column, and then to the at the bottom part of it and beer. Method for the extraction of ethyl alcohol from fusel fractions. It is known that for effective stratification of the water-alcohol mixture in the decanter, the actual content of ethyl alcohol in the liquid should not exceed 34% (40.8% vol.) (Osypenko O. et al., 2013).

Processing of by-products and intermediates in a experimental impurity concentration column in a cyclic mode by methods I, II, III.

The results of the study of the efficiency of processing alcohol-containing fractions enriched with head, intermediate, and terminal alcohol impurities by method I (Figure 3) showed that when mixing phlegm at a temperature of 65 °C and hot hydroselection water at a temperature of 92 °C, the process of mixture stratification in the decanter accelerated, but the quality of the FEAC deteriorated. Higher alcohols of fusel fractions, which were part of the FEAC, retained more water and ethyl alcohol at an increased demulsification temperature. Washing of the FEAC with luther water and extraction of ethyl alcohol in the extractor of the distillation column made it possible to reduce its losses with the impurity concentrate by 8% and increase the concentration of higher fusel oil alcohols by 40% compared to the known method.

Cooling of the phlegm supplied from the dephlegmator to the decanter to a temperature of 20–35 °C according to Method II (Figure 4) allowed for effective separation of the mixture in the decanter, thereby increasing the degree of concentration of head, intermediate, and terminal alcohol impurities by 26, 37, and 40%, respectively. Heating of the water-alcohol liqui free of impurities, which was fed from the bottom of the decanter to the upper plate of the column, with the heat of luther water to a temperature of 90–92 °C made it possible to reduce the specific consumption of heating steam for the processing process.

Dilution of the phlegm from the dephlegmator in the decanter with luther water at a temperature of 10–15 °C to an alcohol concentration of 30–40% vol. in the mixture, lowering the pH of the mixture to 5–5.5, and reducing its temperature from 65–68 to 20–35 °C according to Method III (Figure 5) made it possible to increase the multiplicity of concentration of head, intermediate, and terminal alcohol impurities by 26, 37, and 40% respectively.

The analysis of Table 1 showed that in the process of joint processing of alcohol-containing fractions in a cyclic mode, provided that any of the methods proposed by the authors is used, the concentration of aldehydes (acetaldehyde) in the finished product decreased by 85%, esters by 35%, methyl alcohol by 87%, and fusel oil by 60% compared to the known processing method. This is due to the fact that by prolonging the contact time of vapor and liquid on the plates to 40 s, the degree of extraction of volatile alcohol impurities increased, and by creating and maintaining optimal conditions for liquid separation in the decanter, the multiplicity of concentration of impurities increased significantly.

A comparative analysis of the calculated values (α) and (β) given in Table 2 confirmed that in the experimental column of cyclic action, provided that deep hydroselection of alcohol impurities was carried out, esters were completely removed. In the selected hydraulic mode of operation of the plates, the degree of extraction of aldehydes, higher alcohols of fusel oil and methyl alcohol increased by 40%. At the same time, the multiplicity of concentration of aldehydes and esters increased by 26%, higher alcohols of fusel oil by 40%, and methyl alcohol by 37% compared to the known method. As a result, the physicochemical parameters of rectified ethyl alcohol, which are shown in Table 1, have significantly improved.

Thus, the high efficiency of the innovative methods of processing by-products and intermediates of alcohol production proposed by the authors was proved in production conditions. The use of resource- and energy-saving methods I, II, and III made it possible to eliminate the disadvantages inherent in the known method, to obtain rectified ethyl alcohol with a high degree of purity and to increase its yield by 3.8–4.0% from one ton of conditional starch. At the same time, the loss of alcohol with impurity concentrate decreased by 8%, and the specific consumption of heating vapor in the processing process by 40% (from 20 to 12 kg/dal a.a. introduced to the feed plate) compared to the known method.

Conclusions

1. The known methods of processing by-products and intermediate products of alcohol production do not allow for the joint processing of head and fusel fractions in the impurity concentration column, which works in stationary mode. The inclusion of an additional fusel column requires higher energy costs and increased metal consumption in the distillation plant.
2. The studies have confirmed the high efficiency and expediency of using a joint method of processing fractions enriched with head, intermediate and terminal alcohol impurities

- in the selected technological mode in the impurity concentration column of a cyclic action equipped with scaly plates with a variable free cross section.
3. The use of innovative processing methods makes it possible to increase the yield of rectified ethyl alcohol from 3.5–3.7 to 3.8–4.0% from one ton of conditional starch, reduce the loss of alcohol with impurity concentrate by 8% and reduce the specific consumption of heating steam by 40% (from 20 to 12 kg/dal of a.a introduced to the feed plate) compared to the known method.
 4. Extending the contact time of vapor and liquid on the column plates to 40 s allows for complete removal of esters, increase of the degree of aldehydes, higher alcohols of fusel oil and methanol recovery by 40% and increase of the multiplicity of concentration of head impurities by 26%, higher alcohols by 40% and methanol by 37%.
 5. To increase the degree of concentration of volatile impurities of alcohol, it is advisable to mix the phlegm after the deflagrator and part of the water for hydroselction in a decanter, assuming that the concentration of ethyl alcohol in the mixture should be 30–40% vol.; for effective separation of liquid the temperature should be 20–35 °C and pH 5–5.5.
 6. Maintaining the above-mentioned technological modes in the impurity concentration column of cyclic action and decanter allowed to reduce the concentration of aldehydes in the finished product by 85%, esters by 35%, methyl alcohol by 87%, fusel oil by 60% and to obtain rectified ethyl alcohol with a high degree of purity using innovative methods proposed by the authors.

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Ecological packaging materials for bakery and confectionery products based on a new pectin modification

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Abstract

Keywords:

Biodegradable
Pectin
Modification
Film
Coating
Vapor
permeability

Article history:

Received
25.07.2022
Received in
revised form
20.11.2022
Accepted
1.12.2022

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DOI:

10.24263/2304-
974X-2022-11-3-
5

Introduction. Pectin is advisable to be used for biodegradable film production. There are a lot of types of modified pectin, but its modification potential has not yet been exhausted.

Materials and methods. Pectin, polyvinyl alcohol (PVA, E 1203), glycerol (E 422), oleic acid were used in this study. The vapor permeability of the film was determined according to BS EN 12086:1997. The physical and mechanical properties (strength and elongation) of the films were determined on the TIRAtest-2151 universal testing machine. Infrared (IR) spectroscopy was performed on a Nexus-475 Nicolet device.

Results and discussion. The effectiveness of the pectin modification was confirmed by IR spectroscopy and elemental analysis. Efficiency was confirmed by the modification of pectin, namely, the change in molecular weight and by the appearance of new bonds and/or functional groups. The formation of pectin amide can be judged by the $\nu(\text{C-N})$ band at 1333 cm^{-1} . Unlike the reaction with ammonia product, the formation of salt groups with urea was not clearly visible. The disappearance of the NH_2 -group deformation scissor oscillation band at 1592 cm^{-1} , as well as the shift of the C=O and C-N valence urea vibration bands may indicate the covalent bond formation between urea and pectin. The elemental analysis data indicate that the pectin esterification with ammonia, as well as with urea, took place. The film strength increased from 20.0 to 32.4 MPa and the vapor permeability decreased from 6.1 $\text{mg}/(\text{m}\cdot\text{h}\cdot\text{kPa})$ to 4.3 $\text{mg}/(\text{m}\cdot\text{h}\cdot\text{kPa})$ when content of pectin modified with ammonia in the film increased from 0.5 to 4.5%. The film elongation increased with an increase of the modified pectin content in the film. Pectin modified with urea showed a similar effect on the film properties as pectin modified with ammonia. However, the film containing pectin modified with urea was stronger, which could be explained by the formation of hydrogen bonds between the free urea amino group and OH groups in the polygalactouronic acid. The developed program based on Microsoft Office Access allows determining the biodegradable material composition based on the vapor permeability.

Conclusions. Fourier-transform infrared spectroscopy (FTIR) and elemental analysis confirmed modification of pectin with ammonia or urea. The resulting material could be used to obtain eco-friendly packaging material having better physico-mechanical and barrier properties than original one.

Introduction

The world community is currently determined to reduce the use of the polymer packaging materials. As alternative to conventional synthetic packaging new eco-friendly edible films and coatings that are materials used to wrap or coat food products to extend their shelf life and can be eaten together with the product should be proposed. These new packing materials are biodegradable and are decomposed in natural conditions to CO₂, H₂O and humus, so they do not require a separate collection or certain disposal conditions. Such natural substances as whey proteins, casein, wheat gluten, gelatin, polysaccharides such as starch, pectin, carrageen, alginate, gill, gum, chitosan, cellulose and its derivatives, fatty compounds, such as plant fats, animal fats, and waxes are used for the development of edible films and coatings (Caner, 2005; Díaz-Montes et al., 2021; Hammam, 2019).

It was shown that bread individual packaging and the extra plastic bags, which are used as an additional bread wrapping, leads to accumulation of a significant amount of used packaging materials (Svanes et al., 2018). Meanwhile, pectin, one of the natural polymers, can find an application in the production of biodegradable films for different food including bread (Espitia et al., 2014; Lazaridou and Biliaderis, 2020). Confectionery also usually has individual polymer packaging. Besides, confectionery products have an unbalanced composition with a predominant content of carbohydrates and a minimal content of biologically valuable substances. The adding functional components to the edible coating composition could increase the nutritional value of the products.

For effective use of biodegradable materials as a packaging they must have certain physico-mechanical and barrier properties. Based on our research, native and amidated pectins have insufficient physico-mechanical and barrier properties. The ecological packaging material for sandwiches has been patented in order to extend their shelf life (Patent 5543164 UA, Water-insoluble protein-based edible barrier coatings and films), and the edible material for the products of restaurant establishments against drying, moistening and microbiological spoilage was proposed (Patent 27608 UA, Food sprayed film-forming coating). The authors (Patent 3152 UA, Composition of edible film coating; Patent 45172 UA, Food sprayed film-forming coating) offer various coating composition based on different types of starch and its modification to protect bakery from drying. Biscuits (Panchev et al., 2005) and fondant candies (Patent 70679 A UA, Method for production of fondant candies) can also be protected from drying out with an edible coating. Applying of a film from whey proteins plasticized with sucrose in a 1:1 ratio on the surface of chocolate ensured its stable gloss for a long time (Lee et al., 2002). Cheese-based oriental sweets are better stored in an edible film coating based on kappa-carrageenan, chitosan, zein and whey protein concentrate (Guldás et al., 2010). So, currently, edible films and coatings are used for a limited number of products. It is advisable to expand of the packed products range in such materials and the materials range.

In order to further improve of the biodegradable materials properties, it is advisable to change of the raw materials properties for their production due to its modification. Currently, a number of the main raw materials modifications (natural polymers) are already known, in particular, the proposed enzymatic modification of pectin with pectinmethylesterase obtained from orange juice of the *Valencia* variety (Wicker et al., 2003). Cationic derivatives of pectin were obtained due to the interaction of pectin with 3-chloro-2-hydroxypropyltrimethylammonium chloride in the presence of sodium hydroxide (Fan et al., 2012). The chemical modification of amaranth pectin was investigated (Kostin et al., 2013). Salts of pectin with sodium hydroxide, ammonium and some amines were obtained. Modified products are homogeneous powders, with the exception of diethanolamine. It was established

that the introduction of additional groups into the molecule does not disturb the 4C conformation of the pectin pyranose rings and the α -conformation of glycosidic bonds. This article (Chen, Jun, et al., 2015) attempts to review the information about various methods used for pectin modification, including substitution (alkylation, amidation, quaternization, thiolation, sulfation, oxidation, etc.), chain elongation (cross-linking and grafting) and depolymerization (chemical, physical, and enzymatic degradation). Characteristics and applications of some pectin derivatives are also presented. In addition, the safety and regulatory status of pectin and its derivatives were reviewed.

The authors of the present article proposed a generalized classification for the modification of natural polymers based on the literary sources analysis, which is presented in Table 1.

Table 1

Classification of way modification of natural polymers

| Classification sign | Example |
|----------------------------|--|
| Polymer type | a carbohydrate, a protein |
| Type of modifier | a crosslinker of polymer chains; a carrier of hydrophilic groups; a carrier of hydrophobic groups |
| Type of modification | mechanical (heating under excess pressure (extrusion), heating without excess pressure; biochemical (enzymatic, microbiological); chemical |
| Conditions | a catalyst (available, not available); a solvent (without solvent, water, organic solvent); environment (acidic, neutral, alkaline, in the air atmosphere, O ₂ , N ₂ , He); pressure (excess, atmospheric, vacuum) |

According to the analysis of scientific literature, the most of proposed polysaccharide modification schemes are multistage, complex, require expensive and toxic reagents, which is unacceptable for the food industry. Consequently, the synthetic potential of pectin is far from exhausted.

The aim of the present research was to modify pectin to obtain material for bakery and confectionery eco-friendly packaging materials and study the properties of the resulting product.

Materials and methods

Materials

Pectin (esterification degrees 31.0%, 67.5%), polyvinyl alcohol (PVA, E 1203), glycerol (E 422), oleic acid were used in the present study.

Research methods

Films and coatings based on natural polymers were produced under the same conditions: polyvinyl alcohol (PVA) and the obtained modified pectin were mixed in dry

form, the calculated amount of solvent was added and heated until their complete dissolution and/or swelling. Next, a plasticizer (glycerol) was added and stirred until dissolved. The hydrophobic component (oleic acid) was emulsified after its addition in order to obtain a homogeneous mass of the forming solution of the biodegradable coating and/or film. The films were obtained by casting the film-forming solution (91 cm³) onto a Teflon surface (293 cm²). Complete drying of the film took place in 10-12 hours at room temperature. The coating was obtained by applying of a molding solution on the surface of the confectionery or bakery products.

Modification of pectin

By ammonia. 1.94 g of pectin and 40 cm³ of water were added to a three-necked reactor with a Liebig refrigerator, a 100 °C thermometer, and a dividing funnel. The mixture was stirred at a temperature of 50 °C and 0.72 g of ammonia was added dropwise from a separator funnel. The stirring was continued for 15 hours. After mixing, the resulting solution was evaporated in a porcelain cup. The obtained product in the form of a film was crushed and washed with ethyl alcohol. The product was dried at a temperature of 50 ± 2 °C.

By urea. 1.94 g of pectin and 40 cm³ of water were added to a three-necked reactor with a Liebig refrigerator, a 100 °C thermometer, and a dividing funnel. The mixture was stirred at a temperature of 50 °C and a solution of 3.0 g of urea in 15 cm³ of water was added dropwise. The stirring was continued for 26 hours. After mixing and cooling, the product was filtered and dried at room temperature.

Physical and mechanical properties (strength, MPa; elongation, %) of the films were determined on the TIRAtest-2151 universal testing machine

The vapor permeability of the film was determined according to BS EN 12086:1997. The vapor permeability is a value that is numerically equal to the amount of water vapor in milligrams that passes in 1 hour through a layer of material with an area of 1 m² and a thickness of 1 m, provided that the air temperature on the opposite sides is the same, and the difference in partial pressures of water vapor is equal to 1 Pa according to ASTM E96/E96M-16.

FT-IR. Infrared studies conducted on the device Nexus – 475 firm Nicolet, KBr tablet (Chung et al., 2004). Automated composition calculation of biodegradable material using Microsoft Office Access software was developed.

Results and discussion

Pectin with different esterification degrees

Previous modeling studies have shown that films based only on pectin have insufficient properties as a packaging material, which coincides with the data of other researchers in this field (Mangiacapra et al., 2006). That is why a number of researchers suggest supplementing pectin films with other film formers (Alve et al., 2011; Jo et al., 2005) or clay, CaCl₂ (Kang et al., 2005; Silva et al., 2009).

We proposed to strengthen the properties of the pectin film by introducing an additional film former, namely PVA, since this polymer forms quite strong and transparent films. In

addition, it is known that the combination of pectin and PVA is expedient from the point of view of increasing the biodegradability of PVA (Patent 5646206 USA). The use of PVA increases the viscosity of the film-forming solution, which facilitates its application to the surface of products and allows reducing the consumption of pectin as a more expensive raw material. The given investigated quantitative content of pectin (Table 2) is due to previous model experiments, which showed that with a lower pectin content, the film either does not form or is extremely weak. In addition, if such a molding solution is applied to the surface of the products, the molding solution spreads without forming a coating layer. Under the condition of higher concentrations than given in Table 2, the formed film is difficult to chew because it has a rough structure, which can be explained by the insufficient amount of solvent to form a full-fledged film matrix.

In the composition of the film, we use a plasticizer – glycerol, taking into account the property of pectin to form jelly in the presence of a dehydrating agent, which is glycerol. Glycerol, like sucrose, is necessary for the formation of pectin jelly. In our case, glycerol is preferred to avoid the sweet taste of an edible biodegradable film or coating. Since sucrose will be added in quantities lower than the concentrations at which it exerts a preservative effect, such concentrations will have the opposite effect is a favorable environment for the development of microflora. Oleic acid was used as a hydrophobic component instead of linseed oil for economic reasons. The quantitative content of oleic acid was found by the active experiment method. The experimental results of the physico-mechanical and barrier properties of the pectin-based film are shown in Table 2.

Table 2
Changes in the properties of films depending on the type and quantity of pectin (n=5, p<0.05)

| Pectin content with different esterification degrees, % | | Strength, MPa | Elongation, % | Vapor permeability, mg/(m·h·kPa) |
|---|------|---------------|---------------|----------------------------------|
| 31.0 | 67.5 | | | |
| 0.5 | - | 24.3±2 | 62±1 | 7.0±0.2 |
| 1.0 | - | 29.4±4 | 67±3 | 6.8±0.1 |
| 1.5 | - | 33.4±3 | 71±4 | 6.4±0.4 |
| 2.0 | - | 39.3±4 | 79±4 | 6.0±0.2 |
| 2.5 | - | 40.8±4 | 84±5 | 5.3±0.1 |
| 3.0 | - | 42.7±2 | 90±4 | 5.1±0.2 |
| 3.5 | - | 44.9±4 | 94±3 | 5.1±0.2 |
| 4.0 | - | 46.1±1 | 101±1 | 5.2±0.3 |
| 4.5 | - | 48.4±1 | 113±1 | 5.0±0.2 |
| - | 0.5 | 14.4±1 | 42±2 | 8.1±0.1 |
| - | 1.0 | 18.2±2 | 56±2 | 7.7±0.2 |
| - | 1.5 | 21.6±5 | 70±3 | 7.4±0.2 |
| - | 2.0 | 27.8±3 | 83±4 | 6.9±0.3 |
| - | 2.5 | 34.7±3 | 79±2 | 6.8±0.4 |
| - | 3.0 | 36.8±1 | 72±4 | 6.0±0.1 |
| - | 3.5 | 38.1±4 | 66±3 | 5.6±0.2 |
| - | 4.0 | 40.2±2 | 61±5 | 5.6±0.2 |
| - | 4.5 | 41.7±4 | 70±3 | 5.9±0.4 |

Note: the content of other components in the composition of the film: PVA, 1.5%, glycerol, 2%, oleic acid, 2%, water, the rest.

The obtained data (see Table 2) show that increasing the pectin content, depending on the esterification degree, affects the properties of the films in different ways. It is known that the conditions for the formation of jelly for pectin with different degrees of esterification are different. The advantage of low-esterified pectin is its ability to change to a jelly-like state without a dehydrating agent (sucrose). That is why the strength of films made of low-esterified pectin, under the condition of its minimum content, is greater compared to high-esterified pectin under the same conditions, since only in the presence of 0.5% pectin, a network is already formed, which is the film matrix. The change in the elongation index for films from highly esterified pectin occurs randomly, which is probably due to unfavorable conditions (sucrose absence in the amount of 65%, acid with the required dissociation level, and a sufficient amount of water) for the pectin gel-like state formation under the conditions of film production. The lowest values of vapor permeability are characteristic of films made of low-esterified pectin, since, as already mentioned, the conditions for its transition to a jelly-like state are more favorable, as a result of which a well-developed pectin network is formed, which ensures the necessary level of barrier properties. In addition, free carboxyl groups form hydrogen bonds, which also provide the necessary density of the film matrix to reduce vapor permeability, which is characteristic of low-esterified pectin. It is worth noting that a pectin concentration of more than 2.5% does not cause a significant decrease in vapor permeability, therefore, in order to reduce the use of raw materials, it is advisable to dose 2.5% of low-esterified pectin.

The ability of low-esterified pectin to form hydrogen bonds is confirmed by IR spectra (Figure 1).

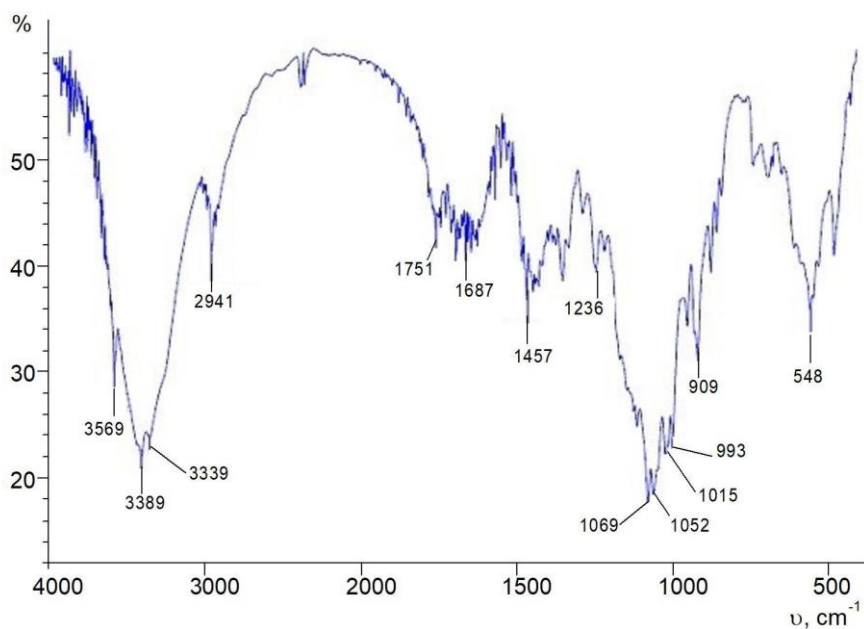
The analysis of the spectra showed (see Figure 1) that the spectrum of highly- esterified pectin has an intense band with three maxima at 3400.56 cm^{-1} , 3316.52 and 3271.70 cm^{-1} , which correspond to the valence νOH vibrations of the pectin glucourone rings. In the IR spectrum of low-esterified pectin (see Figure 1a), there is also an intense band with three maxima at 3568.62 cm^{-1} , 3389.35 and 3338.93 cm^{-1} , but the maximum is located in a more intense oscillations region at 3568.62 cm^{-1} and separated from the other two (3389.35 cm^{-1} and 3338.33 cm^{-1}), corresponds to the OH group valence vibrations of the free pectin carboxyl group, which takes an active part in the formation of hydrogen bonds, which indicates a greater number of hydrogen bonds, and, as a result, a lower esterification degree. Therefore, it is most appropriate to use low-esterified pectin for the production of biodegradable edible films and coatings.

In order to control the pectin esterification degree, especially in industrial conditions, the authors developed an express method, which was used to determine the degree of pectin modification (Shulga et al., 2020).

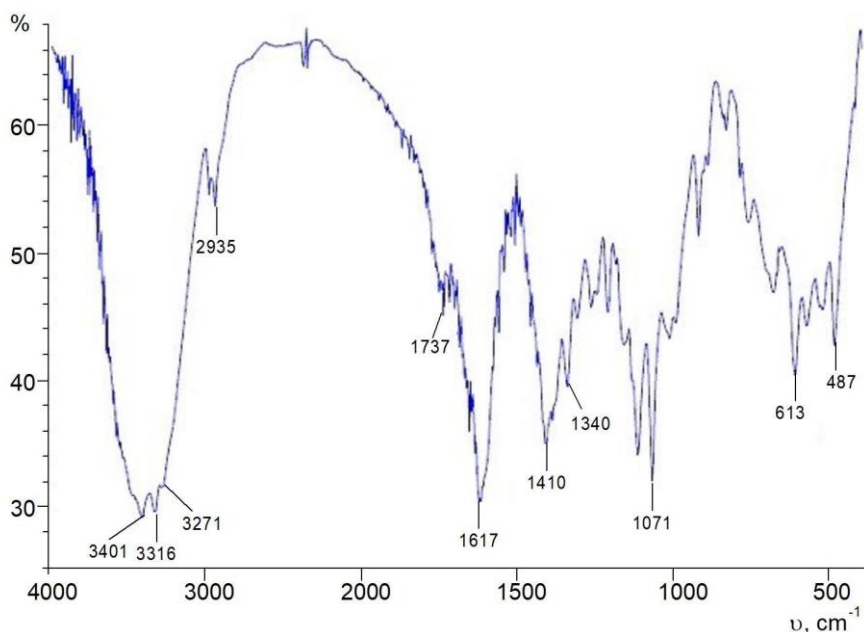
The existing types of pectin do not meet all the requirements as a film former, in particular, pectin films have insufficient barrier properties, so it is advisable to modify the film former (pectin). The following substances were chosen as pectin modifiers: ammonia and urea.

The given substances were chosen for the following reasons: ammonia is a modifier that already allows obtaining amidated low-esterified pectin, but its properties as a modifier have not yet been fully used; urea is an approved food additive E 927b, which is currently not used as a modifier for pectin. In addition, these modifiers are economically available.

The reactions of pectin with ammonia, urea were carried out in an aqueous environment, which is more acceptable than in methyl alcohol (Skoblyia et al., 2004; Synytsya et al., 2003) from their use in the food industry (Mishra et al., 2009). In addition, on the basis of previous studies (Kobilins'kij et al., 2008; 2010) it was found that the interaction of pectin with polyethyleneimine in water led to the formation of amide groups due to the saponification of ester groups.



a



b

Figure 1. IR-spectrums of pectin: a, highly-esterified pectin; b, low-esterified pectin (n=3, p<0.05)

One of the main requirements for the obtained products is the production of film packaging materials from them, which in terms of barrier properties were not inferior to materials based on synthetic polymers. In addition, natural polymers, depending on the thickness of the film, tend to form relatively strong materials.

Pectin modification with ammonia

The qualitative change of pectin can be confirmed by IR spectroscopy. The IR spectra of original pectin and modified pectin (pectinamide) are presented in Figure 2.

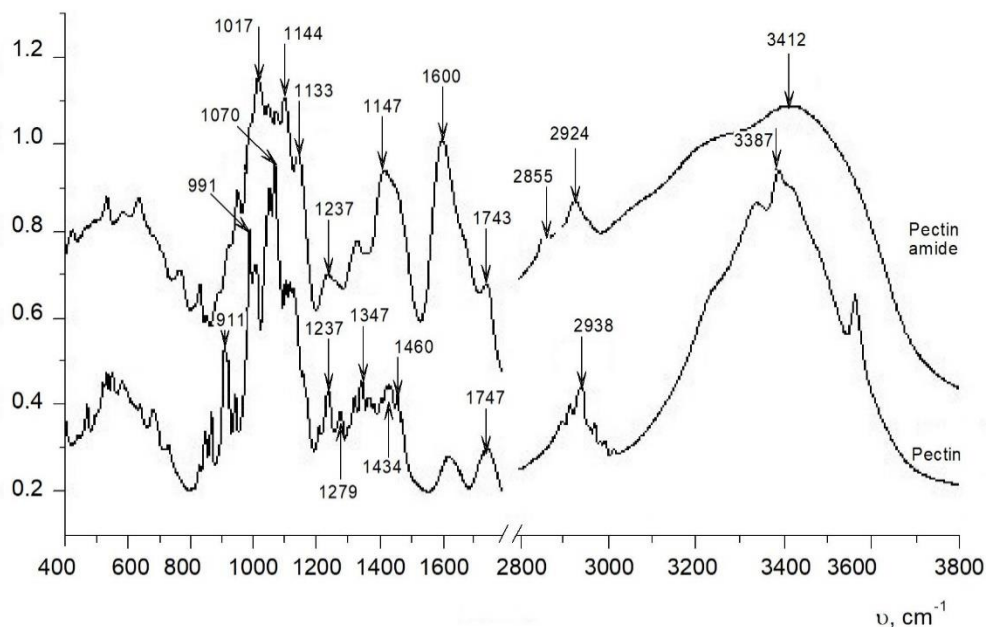


Figure 2. IR spectra of pectin and the product of its interaction with ammonia (n=3, p≤0.05)

The bands of the original pectin (Mishra et al., 2009) can be interpreted as follows: 3387 cm^{-1} $\nu(\text{OH})$, 2938 cm^{-1} $\nu(\text{C-H})$, 1747 cm^{-1} $\nu(\text{C=O})$, 1434 cm^{-1} $\delta(\text{CH}_3)$, bands in the range of 1000-1200 cm^{-1} refer to valence vibrations $\nu(\text{C-C})$ and $\nu(\text{C-O})$ of the pyranose ring, glycosidic bond and alcohol groups. In particular, the band at 1070 cm^{-1} refers to $\nu(\text{C}_3\text{-OH primary})$, 1052 cm^{-1} to C-O-C of the pyranose ring, the band at 1130 cm^{-1} to $\nu(\text{C-O-C})$ of the glycosidic bond, bands at 1237, 1279 cm^{-1} – $\nu_{\text{ac}}(\text{C-O})$ of carboxyl and ester groups, respectively. In the reaction product of the pectin with ammonia, intense bands of 1600 cm^{-1} and 1417 cm^{-1} appear, which relate to asymmetric and symmetric valence vibrations of the ionized carboxyl group COO^- and overlap the C=O and NH bands of the amide group.

The formation of pectin amide can be judged by the $\nu(\text{C-N})$ band at 1333 cm^{-1} . The saponification reaction of the pectin ester groups are indicated by the disappearance of bands at 1279 cm^{-1} and 911 cm^{-1} , which refers to the pendulum oscillations of the $\rho(\text{CH}_3)\text{COOCH}_3$ group.

The elemental analysis data show the pectin esterification with ammonia took place on the basis of a fragment consisting of four galactourone rings containing amide, ammonium, methoxylated and free carboxyl groups. The amount of carbon was found to be 40.175%, calculated to be 40.595%; hydrogen was found to be 4.762%, calculated to be 5.142%; nitrogen was found to be 3.369%, calculated to be 3.789%.

Currently, low-esterified amidated pectin with the help of ammonia is presented on the Ukrainian market, which has a number of advantages compared to high-esterified and low-esterified pectin: gels are thermoreversible, at temperatures below gel formation they retain fluidity during mixing, and are tolerant to a larger range of calcium salt content. In the work, modification with ammonia is proposed, since studies of the modified product have shown that in the presence of an ammonia excess, salt ammonium groups (-COONH₄) are formed, which increase the pectin solubility. If there is a water limited amount in the formulation solution, the increase in solubility will contribute to a more complete formation of the film/coating matrix, which will positively affect their properties. The properties of the film obtained using ammonia-modified pectin are shown in Table 3.

Table 3

Properties of a film with pectin modified with ammonia (n=5, p≤0.05)

| Content of modified pectin, % | Strength, MPa | Elongation, % | Vapor permeability, mg/(m·h·kPa) |
|--------------------------------------|----------------------|----------------------|---|
| 0.5 | 20.0±2 | 84±2 | 6.1±0.3 |
| 1.5 | 23.8±2 | 98±2 | 5.6±0.3 |
| 2.5 | 28.3±2 | 114±3 | 5.1±0.2 |
| 3.5 | 31.2±3 | 128±3 | 4.5±0.2 |
| 4.5 | 33.4±3 | 147±5 | 4.3±0.2 |

Note: the content of other components in the composition of the film: PVA, 1.5%, glycerol, 2%, oleic acid, 2%, water, the rest.

The results show that the strength of the film increases from 20.0 to 32.4 MPa with increasing the content of ammonia-modified pectin in the film composition from 0.5 to 4.5%. The film elongation index increases with an increase in modified pectin in the film composition: it was 147% for sample with a modified pectin content of 4.5%, against 84% with a modified pectin content of 0.5%.

The film vapor permeability decreases with an increase in the content of modified pectin in the composition of the film from 6.1 mg/(m·h·kPa) (pectin content of 0.5%) to 4.3 mg/(m·h·kPa) (pectin content of 4.5%) (Table 3).

The obtained results are explained by the change of free pectin carboxyl groups to amide and salt groups, which increases solubility and allows the formation of a more developed pectin network. Free carboxyl groups that remained after the modification contribute to the formation of hydrogen bonds. The modifications carried out make pectin thermoreversible, which is important in working with it and will reduce the production waste amount.

Pectin modification with urea

The formation salt groups with urea is not clearly visible unlike the reaction with ammonia. The bands at 1453, 1627, 1664 cm⁻¹ can be attributed to ν(C-N), ν(C=O), δ (NH),

δ (NH_2) of the urea fragment (Figure 3). The disappearance of the NH_2 group deformational scissor vibrations band at 1592 cm^{-1} , as well as the shift of the $\text{C}=\text{O}$ and $\text{C}-\text{N}$ valence urea vibrations band may indicate the formation of a covalent bond between urea and pectin. Similarly to the previous product IR spectrum, the band at 913 and 1279 cm^{-1} disappears, which is due to the saponification of ester groups. The band at 1747 cm^{-1} indicates that not all carboxyl groups are involved in the salt bonds formation.

The elemental analysis results indicate the pectin esterification with urea took place on the fragment consisting basis of four galacturonic rings containing imidoamide, methoxy and two free carboxyl groups. Carbon was found to be 40.693% , calculated to be 41.053% ; Hydrogen was found to be 4.074% , calculated to be 4.737% ; Nitrogen was found to be 3.404% , calculated to be 3.684% .

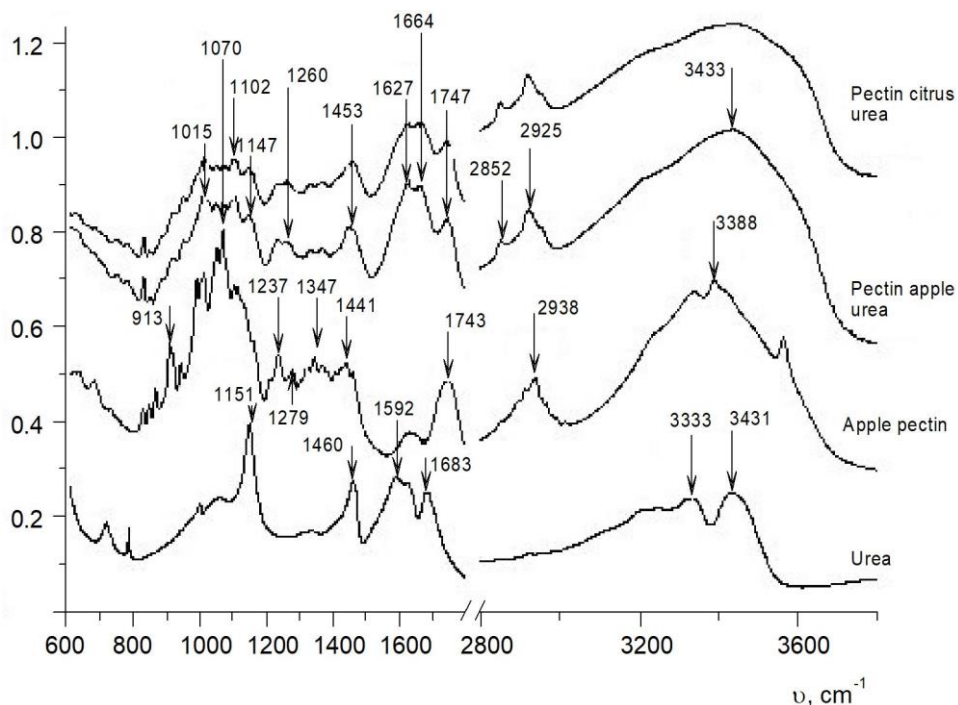


Figure 3. IR spectra of apple pectin, urea and two different pectins with urea products ($n=3$, $p \leq 0.05$)

Urea is used in the films production as a plasticizer that is why the modification of pectin with urea is of particular interest. Therefore, the film former modification with urea will avoid the technological stage is adding a plasticizer.

The pectin modification effect on the properties of biodegradable edible film is shown in Table 4.

Table 4

Properties of a film with pectin modified with urea
(n=5, p≤0.05)

| Content of modified pectin, % | Strength, MPa | Elongation, % | Vapor permeability, mg/(m·h·kPa) |
|-------------------------------|---------------|---------------|----------------------------------|
| 0.5 | 21.8±2 | 81±3 | 6.5±0.3 |
| 1.5 | 26.7±2 | 87±3 | 6.0±0.3 |
| 2.5 | 29.0±2 | 115±5 | 5.7±0.3 |
| 3.5 | 33.4±3 | 129±5 | 5.2±0.2 |
| 4.5 | 35.9±3 | 139±5 | 5.0±0.2 |

Note: the content of other components in the composition of the film: PVA, 1.5%, glycerol, 2%, oleic acid, 2%, water, the rest.

According to the experimental data (Table 4), pectin modified with urea exerts a similar effect as pectin modified with ammonia on the film properties. However, the formed film is stronger, 21.8 MPa (for pectin content of 0.5) (Table 4), against 20.0 MPa with the same pectin content (Table 3), which is explained by the formation of hydrogen bonds between the free urea amino group and OH groups of polygalactouronic acid. This property also leads to a decrease in elongation compared to a film containing pectin modified with ammonia. The vapor permeability value is at the same level as for a film with pectin-amide. The modification also makes pectin thermoreversible.

Conclusions

The obtained products novelty was confirmed by IR spectroscopy and elemental analysis. The elementary link of the pectin modification with urea consists of four galacturonic rings, which contain imidoamide, methoxy and two free carboxyl groups. The elementary link of the pectin modification with ammonia consists of four galactourone rings, which contain amide, ammonium, methoxylated and free carboxyl groups. Urea modification gives pectin thermal reversibility, the resulting modification products meet the level of food safety. The obtained new modifications of pectin will make possible to produce ecological packing materials with improved physico-mechanical and barrier properties.

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Antioxidant properties of water-alcohol infusions of tea-herbal compositions based on yerba mate

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Abstract

Keywords:

Yerba mate
Ilex
paraguariensis
Tea-herbal
Alcohol
Beverage
Antioxidant

Introduction. The aim of the research was to determine the antioxidant capacity of water-alcohol infusions of tea-herbal compositions based on yerba mate (*Ilex paraguariensis*) and evaluate their potential to be used in production of alcoholic beverages.

Materials and methods. Vegetable raw materials, namely *Ilex paraguariensis* and *Camellia sinensis* (fermented tea; partially fermented tea; unfermented tea) were used in the study. A water-alcohol mixture, 40% (alcohol by volume), was used as control. The antioxidant capacities of water-alcohol infusions of tea-herbal compositions were determined using the method of redox and pH-metry; sensory indicators were evaluated by the method of scoring with the definition of a complex indicator of quality.

Results and discussion. The antioxidant capacity of water-alcohol infusions of tea-herbal compositions was determined: active acidity, pH, ranging from 5.5 to –6.2 units pH; redox potential varied from 101.00 to 157.70 mV; recovery energy of infusions changed in diapason from 112.88 to 145.76 mV and the energy of reduction/oxidation of plant raw materials ranged from 28.34 to 61.22 mV. Water-alcohol infusions of tea-herbal compositions based on mate are characterized by high recovery energy 61.22 mV of and such indicators as: score, 9.63 points. The color tea-herbal compositions was light brown, the aroma was woody, the taste was sour-bitter, with a long-lasting bitter aftertaste, so they could be recommended to be used in the technology of alcoholic beverages in small quantities.

In the process of preparation of tea-herbal compositions, there was an increase in the indicators of the sensory evaluation in the mixtures based on tea/yerba mate in ratio 75 to 25: fermented tea/mate, 9.67 points; partially fermented tea/mate, 9.68 points; unfermented tea/mate, 9.71 points. A recipe composition of alcoholic beverages with a following composition has been developed: water-alcohol infusion of tea-herbal composition,%: fermented tea/mate, or partially fermented tea/mate, or unfermented tea/mate (in ratio 75:25), 38.5; brandy, 7.5; vanillin (1:10), 0.01; sugar syrup (65.8%), 53.1; citric acid, 0.3, «Caramel E 150», 0.6; ethyl alcohol and prepared water to ensure the strength of 20%.

Conclusion. The use of water-alcohol infusions of tea-herbal compositions based on yerba mate (*Ilex paraguariensis*), which have increased antioxidant characteristics and sensory indicators, was proposed for restaurant industry technology for the production of alcoholic beverages.

Article history:

Received 16.07.2022

Received in revised
form 19.10.2022

Accepted 1.12.2022

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DOI:

10.24263/2304-
974X-2022-11-3-6

Introduction

Multi-component alcoholic drinks, namely infusions on plant materials, attract attention with the biologically active substances they contain. In the production of such alcoholic beverages natural plant extracts from herbaceous plants, wild fruits and berries, which have a pleasant taste and aroma, and are a rich source of biologically active compounds such as vitamins, minerals, polyphenols, and organic acids are used (Bravo et al., 2007; Gullón et al., 2018; Pluta-Kubica et al., 2020; Rebocho et al., 2022).

It is known that *Ilex paraguariensis* contains various compounds with high antioxidant activity (Dos Santos et al., 2017). Water-alcohol infusions obtained by extraction from dried leaves of this plant with a water-alcohol mixture possessed high antioxidant activity (Dos Santos et al., 2017). So, the creation of water-alcohol tinctures of tea-herbal compositions based on yerba mate (*Ilex paraguariensis*) containing substances with antioxidant properties will improve the quality and nutritional value of new alcoholic drinks.

The aim of the present research was to determine the antioxidant capacity of water-alcohol infusions of tea-herbal compositions based on yerba mate (*Ilex paraguariensis*) and evaluate their potential for restaurant industry technology for the production of alcoholic beverages. The creation of alcoholic beverages by introducing water-alcohol infusions of tea-herbal compositions with antioxidant properties allows restaurants to prepare new products that distinguish them from competitors and create a favorable image.

Materials and methods

Materials

The study used samples of plant raw materials, namely, *Ilex paraguariensis* and *Camellia sinensis* (fermented tea; partially fermented tea; unfermented tea). As a control sample a 40% (alcohol by volume) water-alcohol mixture was used.

Water-alcohol infusions preparation

Drying of plant raw materials was performed in order to reach a moisture content of 6–8%. Each dried plant raw materials, 4 g, and 100 ml of a water-alcohol mixture 40% (alcohol by volume) were placed in dark glass bottles. The vials were capped and placed in a dry-air thermostat DUROCELL 55 (BMT, Brno) for 48 hours at 40 °C. The resulting infusions were cooled at 20 °C, filtered and stored at 4°C.

Determination of active acidity and redox potential

The active acidity was measured on a pH-meter «pH-150 MA» with a combined glass electrode «ESC 10601/4». Redox potential was measured on the pH-meter «pH-150M», by measuring the potential with a platinum redox electrode «ERP-105».

To evaluate the antioxidant properties of the water-alcohol plant extracts, the method, which is based on the difference of redox potentials in water-alcohol solutions, was used. This method allows to determine the total antioxidant activity of liquid products including complex mixtures and multifunctional antioxidants (Khareba et al., 2021; Kuzmin et al., 2020; 2021).

Determination of redox potential from hydrogen display in alcohols infusions of plant raw materials

For water-alcohol mixture, the relationship between hydrogen index (pH) and redox potential (Eh) was determined. It was shown that the change of pH of the water-alcohol mixture by 1 unit leads to a change in redox potential by 42 mV (Kuzmin et al., 2020):

$$Eh_{\min} = 502 - 42 \cdot \text{pH}, \text{ mV}, \quad (1)$$

In the range of values of the hydrogen index of 2.0–11.0 pH units for the water-alcohol mixture redox potential varies in the range of Eh_{\min} 418.0–40.0 mV (Kuzmin et al., 2020).

The obtained values of the redox potential of the water-alcohol mixture Eh_{\min} were correlated with the actually measured values of the redox potential of alcohol infusions (RE_{inf}) from plant raw materials by the platinum electrode (Eh_{act}), which characterizes the difference of these values (RE_{inf}) (Kuzmin et al., 2020):

$$RE_{\text{inf}} = Eh_{\min} - Eh_{\text{act}}, \text{ mV}, \quad (2)$$

The energy of reduction/oxidation process of plant raw materials (RE_{plant}) is determined by the difference between of alcohol infusions from plant raw materials (RE_{inf}) and solvent (control) (Kuzmin et al., 2020):

$$RE_{\text{plant}} = RE_{\text{inf}} - RE_{\text{sol}}, \text{ mV}$$

According to the results of research, an optimized method to assess the antioxidant capacity of alcohol infusions from plant raw materials has been developed (Kuzmin et al., 2020).

Sensory evaluation

The sensory evaluation (S. e.) of the obtained infusions was carried out with a point scale with the involvement of highly qualified and experienced experts in the field of alcoholic beverages assessment.

Results and discussions

Antioxidant capacity and sensory evaluation of water-alcohol tea-herbal infusions

The physico-chemical and sensorial indicators of obtained water-alcohol tea-herbal infusions are presented in Table 1.

Table 1

Characteristics of water-alcohol infusions

| Parameters | Extractant (water-alcohol mixture) | Water-alcohol infusion of | | | |
|--------------------------|--|---------------------------|----------------------------|--------------------|--------|
| | | fermented tea | partially fermented tea | unfermented tea | mate |
| Active acidity, pH | 5.63 | 5.51 | 5.91 | 6.20 | 5.77 |
| Eh_{\min} , mV | 265.54 | 270.58 | 253.78 | 241.60 | 259.66 |
| Eh_{act} , mV | 181.00 | 157.70 | 119.50 | 101.00 | 113.90 |
| RE_{inf} , mV | 84.54 | 112.88 | 134.28 | 140.60 | 145.76 |
| RE_{plant} , mV | 0.00 | 28.34 | 49.74 | 56.06 | 61.22 |
| S.e., points | 9.50 | 9.61 | 9.64 | 9.67 | 9.63 |

Note: Eh_{\min} , the minimum theoretical value of redox potential; Eh_{act} , actual value of redox potential; RE_{inf} , recovery energy of infusions; RE_{plant} , the energy of reduction/oxidation of vegetable raw materials; S.e., sensory evaluation indicators.

A water-alcohol mixture was used as a solvent with pH 5.63; $E_{h_{min}}$, 265.54 mV; $E_{h_{act}}$, 181.00 mV; RE, 84.54 mV; S.e. 9.50 points (color – colorless; aroma – alcoholic; taste – moderately burning, empty). For the fermented tea water-alcohol infusions the pH reached the value of 5.51, while in the case of partial fermented tea this value was 5.91 and for unfermented tea – 6.20 pH units. It can be concluded that the tea degree of oxidation/fermentation contributes to the change in the pH level. It is known that unfermented tea (green, white tea) is not subject to oxidation, or low oxidation, while partially fermented tea (red, yellow tea) are subjected to partial oxidation and fermented tea (black tea) is completely oxidized. This is explained by the presence of organic acids in tea that undergo changes during the fermentation process (Yu et al., 2022). The value of RP ($E_{h_{min}}$ for water-alcohol tea-herbal infusions) was obtained, which has a value from 241.60 (unfermented tea) to 270.58 mV (fermented tea); the actual measured RP of water-alcohol tea-herbal infusions ($E_{h_{act}}$) – from 101.00 (unfermented tea) to 157.70 mV (fermented tea).

The regenerative capacity (recovery energy, RE_{inf}) of water-alcohol tea-herbal infusions ranged within the limits: from RE_{inf} , 112.88 for fermented tea to RE_{inf} , 145.76 mV for mate tea. The reduction/oxidation energy of tea-herbal plant materials (RE_{plant}) relative to the solvent – water-alcohol mixture was in the range of values from 28.34 (fermented tea) to 61.22 mV (mate tea). It can be concluded that water-alcohol tea-herbal infusions are depending on the activity of plant raw materials and have a regenerative capacity (over 0 mV) – 100% of samples. In addition to physical and chemical indicators, water-alcohol tea-herbal infusions had excellent sensory scores (S.e.), which depend on the degree of tea fermentation. The fermented tea obtained a score of S.e., 9.61 points (color – dark brown; aroma – tea, woody; taste – moderately burning, very astringent), while the unfermented tea registered a value of S.e., 9.67 points – (color – brownish brown; aroma – tea, fragrant; taste – sour-bitter, astringent).

At the first stage, it can be concluded that the sample of water-alcohol tea-herbal infusion of unfermented tea is the most promising, which has a high sensory score of 9.67 points and can be recommended in the technology of alcoholic beverages.

Antioxidant and sensory evaluation of the water-alcohol infusion of mate

Biological effect of tea depends on the degree of its oxidation/fermentation, which is explained by the change in the antioxidant activity of chemical compounds present in tea, especially flavonoids and phenolic acids (Oh et al., 2013; Sentkowska and Pyrzynska, 2018; Silveira et al., 2014; Zielinski et al., 2014). The water-alcohol infusion of mate, prepared from yerba mate (*Ilex paraguariensis*), had the following physical and chemical characteristics: pH 5.77; $E_{h_{min}}$ 259.66 mV; $E_{h_{act}}$ 113.90 mV; RE_{inf} 145.76 mV; RE_{inf} 61.22 mV. Comparing this characteristics with those of the water-alcohol infusions of tea, depending on the degree of fermentation, allows us to state the following: the antioxidant capacity of the water-alcohol infusion of mate (RE_{inf} 145.76 mV) is 54% higher compared to the water-alcohol infusion of fermented tea (RE_{inf} 112.88 mV); 19% higher compared to the water-alcohol infusion of partially fermented tea (RE_{inf} 134.28 mV); 8% higher compared to the water-alcohol infusion of unfermented tea (RE_{inf} 140.60 mV). The antioxidant capacity of raw mate (RE_{plant} 61.22 mV) is 23% higher compared to fermented tea (RE_{plant} 28.34 mV); 8% higher compared to partially fermented tea (RE_{plant} 49.74 mV); 4% higher compared to unfermented tea (RE_{plant} 56.06 mV). This can be explained by the presence of several biologically active compounds: caffeic acid ← hydroxycinnamic acids ← phenolic acids ← simple phenols ← phenolics (Anesini et al., 2012; Riachi et al., 2018; Souza et al., 2011; 2015; Yang and Liu, 2013; Zielinski et al., 2014); gallic acid ← hydroxybenzoic acids ← phenolic acids ← simple phenols ← phenolics (Zielinski et al., 2014); catechins; epicatechin; rutin ← flavonols ← flavonoids ← polyphenols

← phenolics (Anesini et al., 2012; Bravo et al., 2007; Mazzafera, 1997; Zielinski et al., 2014); procyanidin B2 ← condensed ← tannins ← non-flavonoids ← polyphenols ← phenolics (Zielinski et al., 2014); particularly caffeoyl derivatives ← chlorogenic acids (Anesini et al., 2012; Bravo et al., 2007; Marques and Farah, 2009; Wan et al., 2021; Zang et al., 2003); quercetrin; caffeine ← methylxanthines ← purine alkaloids (Zielinski et al., 2014).

Therefore, water-alcohol infusion of tea can be recommended in the technology of alcoholic beverages in a smaller amount than mate infusions, due to specific sensory indices: color – light brown; aroma – woody; taste – sour-bitter, with a long-lasting bitter aftertaste (S.e. 9.63 points). Similar results were stated by Godoy et al. (2013), who characterized the sensory properties of mate infusions: color – light green; aroma – specific; taste – characteristically bitter, reminiscent of strong green tea.

Antioxidant capacity of water-alcohol tea-herbal infusions

The potential of creating tea-herbal compositions based on ready-made dried mixtures have been confirmed by many authors (Alaşalvar and Çam, 2019; Tülek et al., 2020). A functional tea-herbal composition is perfect for everyday consumption, rich in vitamins and microelements, does not contain caffeine and allows to get a high content of microelements necessary for a person (Chen et al., 2019; Feng et al., 2019; Guo et al., 2019).

Water-alcohol tea-herbal infusions and their combinations are promising for restaurants in the production of alcoholic beverages, which allow to obtain increased antioxidant characteristics and positive sensory scores (Figure 1–3). This is supported by the research of Bravo et al., 2007, where is proved that mate has slightly higher antioxidant activity than black tea, but lower than green tea. At the same time, content of total phenolic compounds of the *Ilex paraguariensis* extract is higher than that of green tea (Bravo et al., 2007; Gugliucci et al., 2009; Lunceford and Gugliucci, 2005; Zielinski et al., 2014). This confirms the ability to inhibit the formation of *Ilex paraguariensis* glycation end products compared to green tea (Lunceford and Gugliucci, 2005) and to prevent lipid peroxidation (Barg et al., 2014). While individual phenolic compounds: gallic acid, epicatechin, procyanidin B2 and quercitrin are present only in *Camellia sinensis* teas (Zielinski et al., 2014).

The physicochemical and sensory evaluation indicators of water-alcohol infusions of tea-herbal compositions (fermented tea; partially fermented tea; unfermented tea; mate) are given depending on the mass fraction of their mixtures (ω , %) in steps of 25% (Figure 1–3), with further modeling of the rational composition of water-alcohol infusions for the production of high-quality alcoholic beverages.

It was established that the existing combinations (ω , % 100/0; 75/25; 50/50; 25/75; 0/100) fermented tea/mate (Figure 1); partially fermented tea/mate (Figure 2); unfermented tea/mate (Figure 3) make it possible to expand the ranges of the rational composition of alcohol infusions of tea-herbal compositions when modeling a qualitative composition.

According to the research results, it was established that in the process of mixing tea-herbal compositions, there is an upward of sensory evaluation scores – for mixtures ω ,% 75/25: for fermented tea/mate – S.e. 9.67 points (Figure 1, f), partially fermented tea/mate – S.e. 9.68 points (Figure 2, f); unfermented tea/mate – S.e. 9.71 points (Figure 3, f).

The developed composition of the tea and herbal mixture ensures the obtaining a new product with pleasant, harmonious sensory properties and high uniformity of distribution of flavoring and biologically active substances. This confirms the potential of using *Ilex paraguariensis* for the production of beverages as it was proposed in the studies (Esmelindro et al., 2004; Mesquita et al., 2021; Souza et al., 2015).

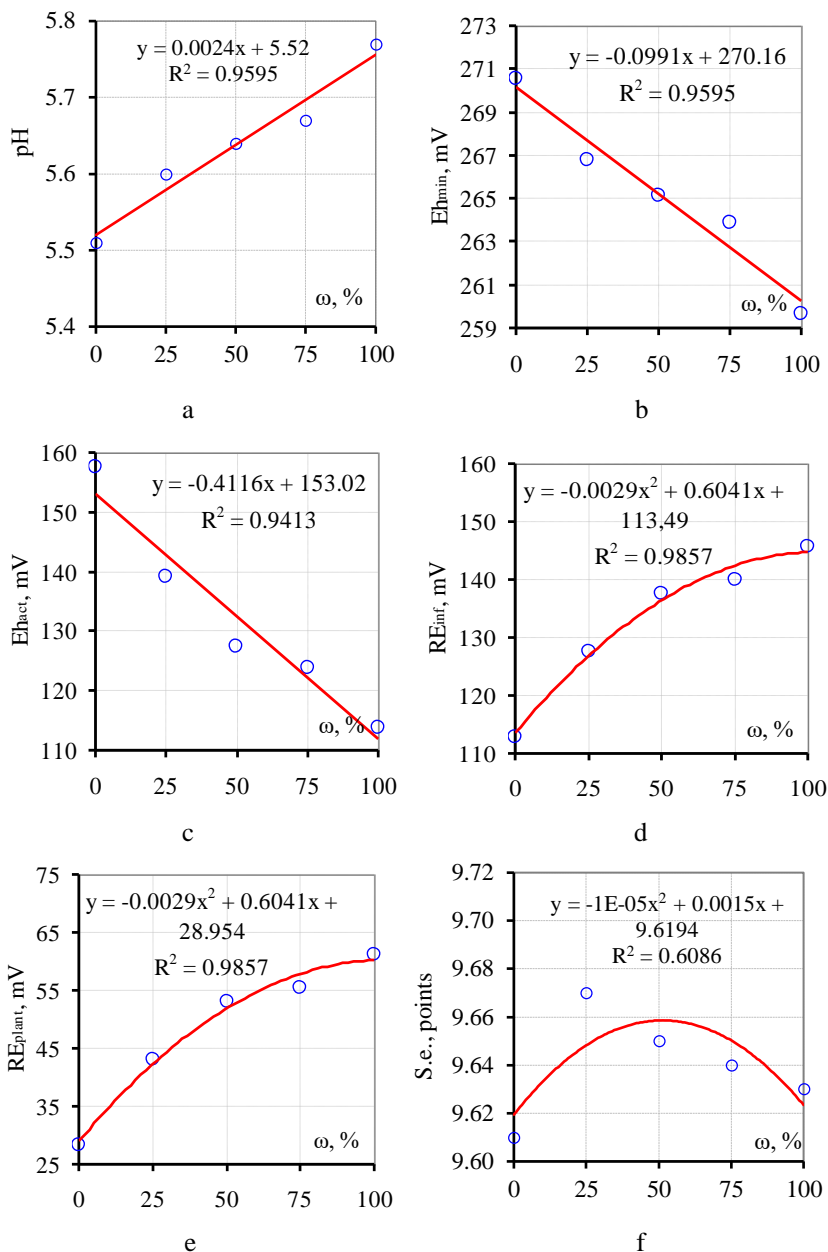


Figure 1. Characteristics of water-alcohol infusions of tea-herbal compositions depending on the mass fraction of fermented tea and mate (ω):

a, active acidity (pH); b, the minimum theoretical value of RP (E_{hmin}); c, actual measured of RP (E_{hact}); d, recovery energy of infusions (RE_{inf}); e, the energy of reduction/oxidation of vegetable raw materials (RE_{plant}); f, sensory evaluation indicators (S.e.); combination of fermented tea/mate (ω , %, 100/0; 75/25; 50/50; 25/75; 0/100).

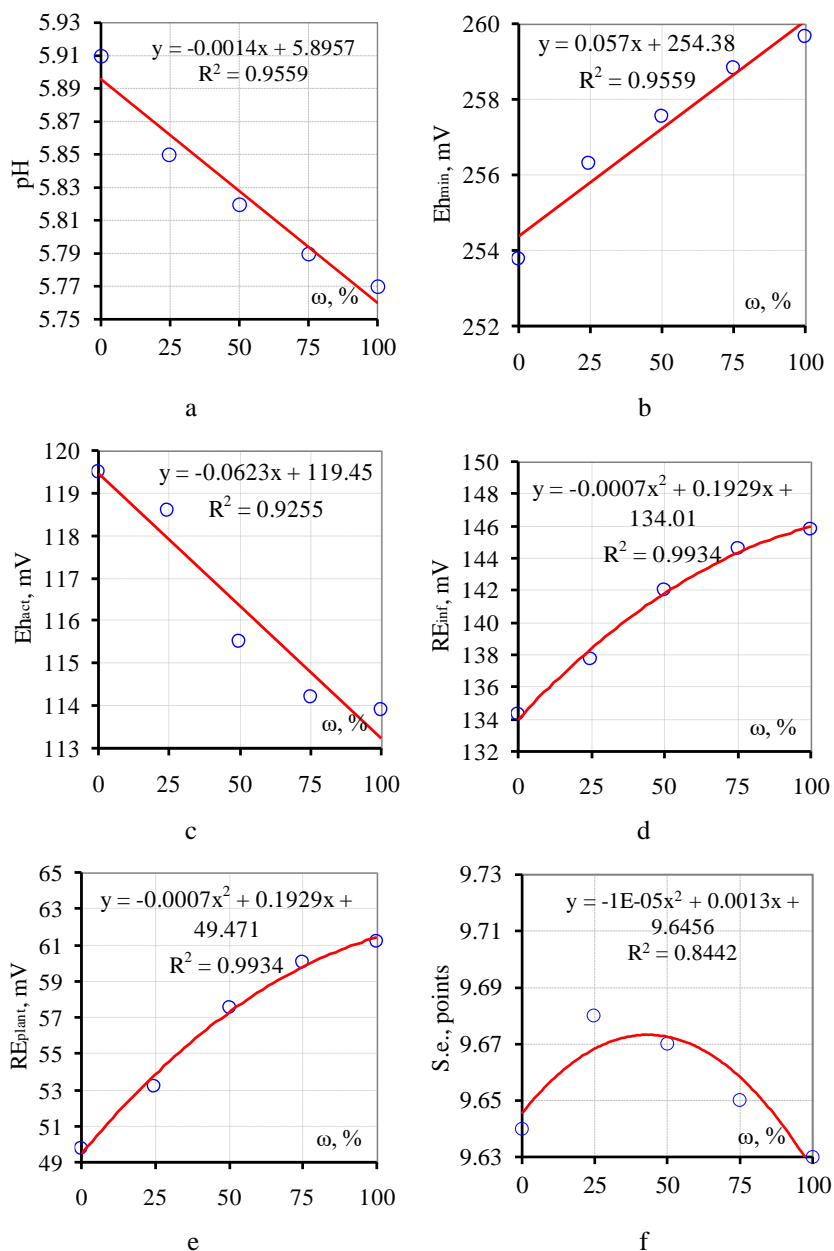


Figure 2. Characteristics of water-alcohol infusions of tea-herbal compositions depending on the mass fraction of partially fermented tea and *mate* (ω):
a, active acidity (pH); b, the minimum theoretical value of RP (E_{hmin}); c, actual measured of RP (E_{hact}); d, recovery energy of infusions (RE_{inf}); e, the energy of reduction/oxidation of vegetable raw materials (RE_{plant}); f, sensory evaluation indicators (S.e.);
partially fermented tea/*mate* combinations (ω , %, 100/0; 75/25; 50/50; 25/75; 0/100).

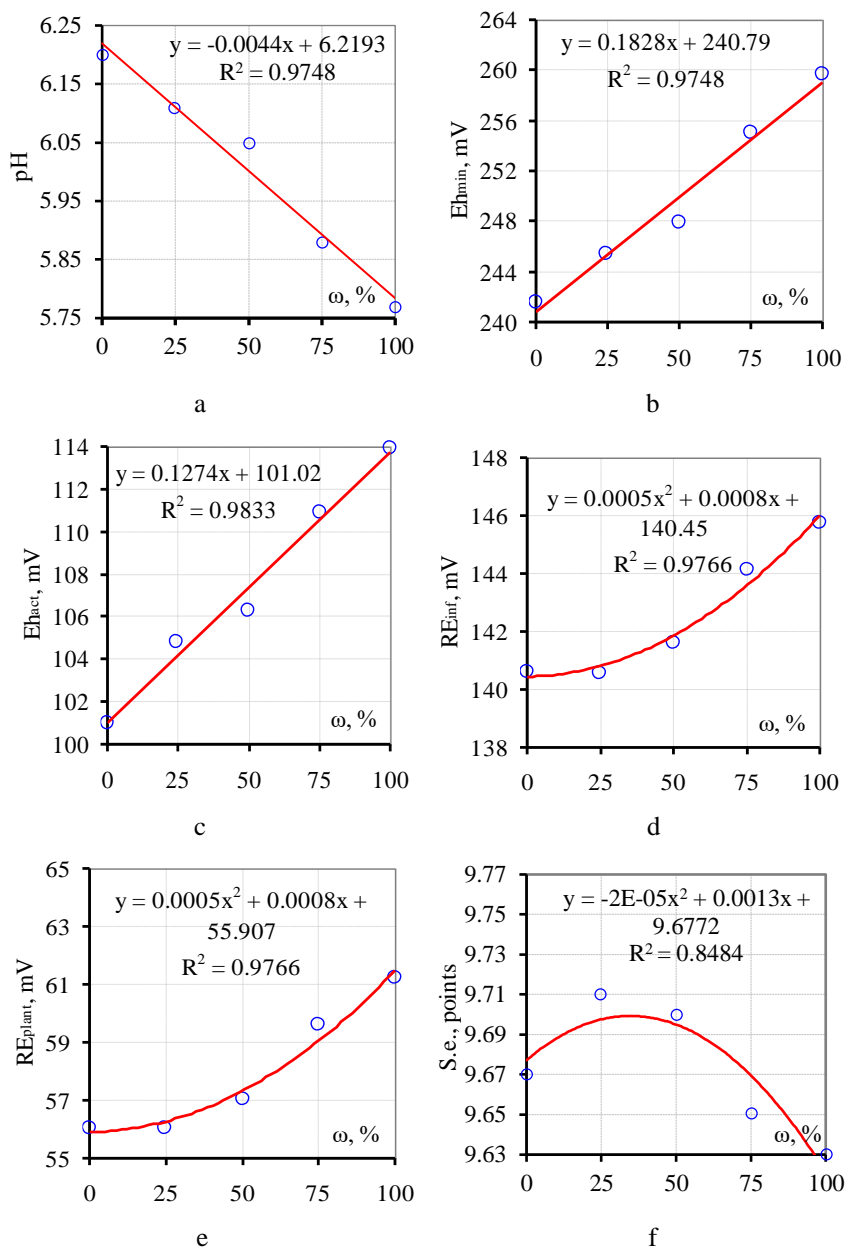


Figure 3. Characteristics of water-alcohol infusions of tea-herbal compositions depending on the mass fraction of unfermented tea and mate (ω):

a, active acidity (pH); b, the minimum theoretical value of RP (E_{hmin}); c, actual measured of RP (E_{hact}); d, recovery energy of infusions (RE_{inf}); e, the energy of reduction/oxidation of vegetable raw materials (RE_{plant}); f, sensory evaluation indices (S.e.); unfermented tea/mate combinations (ω ,% 100/0; 75/25; 50/50; 25/75; 0/100).

Tea-herbal compositions

As a result of the conducted research, the composition of an alcoholic drink was proposed. In the basic recipe compositions of fermented tea/mate, or partially fermented tea/mate, or unfermented tea/mate (ω , %, 75/25) water-alcohol infusions, were added, which allows increasing the redox and consumer properties of the finished product.

To obtain the new alcoholic beverage, the following was used: water-alcohol infusion of tea-herbal composition (fermented tea/mate, or partially fermented tea/mate, or unfermented tea/mate ω ,% 75/25) – 38.49%, brandy – 7.54%, vanillin – 0.01%, sugar syrup (65.8%) – 53.08%, citric acid – 0.28%, «Caramel E 150» – 0.6%. Water-alcohol infusions were prepared based on 20% (alcohol by volume) (Figure 4).

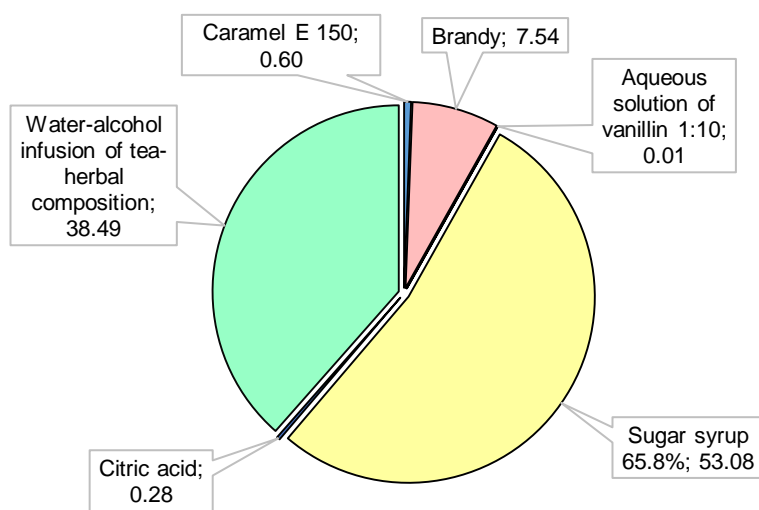


Figure 4. Blending of alcoholic beverage, %

It can be argued that the range of alcoholic beverages and its variety are combined with the possibility of mixing alcohol with many ingredients. Thanks to the different ratio of tea-herbal compositions, new flavors appear that are completely different from each other, as well as various useful properties (Khareba et al., 2021; Kuzmin et al., 2020; 2021). But among all the useful properties, the main thing will be to change the redox reactions (Gullón et al., 2018). The developed composition of the tea and herbal mixture ensures the obtaining of a new product with pleasant, harmonious sensory properties.

Conclusions

Based on the performed theoretical and experimental studies, the following conclusions can be drawn:

1. It was found that the values of the antioxidant capacity of water-alcohol infusions of tea-herbal compositions: active acidity was in the range from 5.5 to 6.2 pH units; RP ($E_{h_{act}}$), 101.00-157.70 mV; recovery energy of infusions (RE_{inf}), 112.88-145.76 mV;

- the energy of reduction/oxidation of plant raw materials (RE_{plant}), 28.34-61.22 mV.
2. The high recovery energy (61.22 mV) of tea herbal infusions based on mate makes them promising for restaurants in the production of alcoholic beverages and in the production of alcoholic beverages. According to the organoleptic evaluation, the mixtures differ in light brown color, woody aroma, sour-bitter taste with a long-lasting bitter aftertaste.
 3. In order to obtain tea herbal infusions based on mate (*Ilex paraguariensis*), the optimal blending ratio has to be: fermented tea/mate (ω , %, 75/25), partially fermented tea/mate (ω , %, 75/25) unfermented tea/mate (ω , %, 75/25).
 4. A recipe composition of alcoholic beverages with a rational composition has been developed: water-alcohol infusion of tea-herbal composition (fermented tea/mate, or partially fermented tea/mate, or unfermented tea/mate ω , %, 75/25) – 38.49%, brandy – 7.54%, vanillin 1:10 – 0.01%, sugar syrup (65.8%) – 53.08%, citric acid – 0.28%, «Caramel E 150» – 0.6%, ethyl alcohol and water are prepared – based on the strength of 20%.

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Chemical composition of peatland small cranberry (*Vaccinium oxycoccus*) for potential use as functional ingredient

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Abstract

Keywords:

Cranberry
Vaccinium oxycoccus
Antioxidant
Polyphenol
Ascorbic acid
Quercetin

Article history:

Received
12.05.2022
Received in
revised form
16.08.2022
Accepted
1.12.2022

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DOI:

10.24263/2304-
974X-2022-11-
3-7

Introduction. The aim of the present study was to determine, for the first time, the small cranberries (*Vaccinium oxycoccus*) chemical composition depending on growing soil.

Materials and methods. The analyses were made on ripe fruits of the plant, harvested from Romania, Suceava county, Coşna commune, in a peat area. The mineral content was determined using a coupled-mass spectrometer (ICP – MS). DPPH method was used for antioxidant activity determination. Folin Ciocalteu method and HPLC analysis were used for polyphenol content determination.

Results and discussion. A value of 84.1% was obtained for fruits' moisture content, close to the values found in other studies. For ash, a relatively low value of 1.38% was obtained that shows a low mineral content, corresponding to the low mineral content of the soil. However, the mineral content of the analyzed fruits is higher than that reported by other studies. For most of the elements there was a positive correlation between mineral content in fruits and soil. A significant amount of calcium was observed in the studied cranberries, close to the average means reported in other studies. Magnesium falls within the limits determined in other studies, and the copper content as well. The contents of manganese, iron and zinc were lower than in other studies. The contents of arsenic, mercury and stibium were below the maximum approved limits and lead is under the detection limit. Regarding the antioxidant capacity, the inhibiting percent of free radicals and total content of polyphenols is higher in aqueous extract than in the ethanolic extract and medium content in the studied fruits, in comparison with other reported data: 340.78 mg/100g in aqueous extract and 254.20 mg/100g in ethanolic extract. According to the results obtained by different authors, the total amount of polyphenols is significantly higher in the wild fruits of *Vaccinium oxycoccus*, as compared to grown cultivars.

Regarding to polyphenols, a high content of quercetin, 0.39 mg/100g, and myricetin, 0.23 mg/100g, is noteworthy. In the ethanolic extracts, chlorogenic acid, 0.42 mg/100 g, and p-hydroxybenzoic acid, 0.41 mg/100 g, appear, close to numbers reported in other studies. However, the presence of rosmarinic acid, 0.12 mg/100g, was observed, which has not been reported previously. In the benzene extract, p-coumaric acid appears, 0.27 mg/100 g. Vitamin C present in the peatland small cranberries, 5.98 mg/100g, contributes to its antioxidant activity.

Conclusions. According to results of the present study, the chemical composition of peatland small cranberries from Romania was close to those obtained in studies on cranberries from other geographic regions, and may be considered as fruit with high antioxidant activity.

Introduction

Peatland small cranberry (*Vaccinium oxycoccus*) is a plant from *Vaccinium* genus from *Ericaceae* family, which includes over 450 species from Europe, North America, Central America, Japan and Asia, Central and South-Eastern Africa, Madagascar (Mabberley et al., 1997). Different blueberries species (*Vaccinium myrtillus*, *V. ashei*, *V. angustifolium*, *V. corymbosum*), cranberries (*V. macrocarpon*, *V. oxycoccus*), huckleberry (*V. ovatum*, *V. parvifolium*), lingonberry (*V. vitis-idaea*) are the most known berries of this genus (Jurikova et al., 2018). The most known cranberry, the big cranberry, called American cranberry (*V. macrocarpon*), originates from the eastern and central North America, including Canadian Eastern territory and found in the highlands moors from North East and Great Lakes of United States (Česonienė et al., 2016). Its fruits Its fruits have been used in local medicine from the XVI century or even earlier (Narwojsz et al., 2019). The European relative of the big cranberry less known and studied is small cranberry, *V. oxycoccus*, with a larger geographical distribution.

Regarding the taste, big and small cranberries accumulate components with similar aroma. In total, between 40 and 70 aromatic substances were detected in big and small berries, meanwhile the fruits of the small cranberry have 4 to 5 times higher concentration of these substances than fruits of big one (Česonienė et al., 2016). The antioxidant activity (Ehala et al., 2005; Jurikova et al., 2018), anticancer activities (Masoudi and Saiedi, 2017), anti-obesity (Jurikova et al., 2018; Kowalska et al., 2014; 2015), cardioprotective (Nemzer et al., 2022) effects and urinary tract protection (Canja et al., 2016, Jurikova et al., 2018) of *Vaccinium oxycoccus* has been shown.

The small cranberries (*Vaccinium oxycoccus*) were gathered on peatlands from the North of Carpathian Mountains. The aim of the present study was to determine the small cranberries (*V. oxycoccus*) chemical composition, particularly the content of moisture, ash, trace elements, nitrites, polyphenols, and vitamin C, as well as their antioxidant activity, and to compare the present paperwork results with the those from other studies on cranberries grown on different areas.

Materials and methods

Materials

Plants harvested in Romania, Suceava County, Coșna commune were used from a peatland area, situated at 47.375188 latitude and 25.166790 longitude, stereo GPS coordinates 70 x = 652942,481, y = 512680,436, approximately 860 altitude (Figure 1, 2).

Ripe berries used for the study were harvested during September – October. Soil samples were taken from the same area to determine ash and minerals contents.

Determination of moisture content

The moisture content was determined by weighing berries sample, dried in oven till the mass remained constant. The moisture content was calculated by the following formula:

$$C, \% = (m_S - m_{DS}) \cdot 100 / m_S,$$

where m_S is sample mass before drying, g; m_{DS} is sample mass after drying, g.



Figure 1. Harvest area of *Vaccinium oxycoccus*.



Figure 2. *Vaccinium oxycoccus* flowers



Figure 3. *Vaccinium oxycoccus* - ripe cranberries

Determination of ash

To determine ash content, fruit and soil samples were calcinated at 800 °C using a Nabertherm LE 2/11/R6 Muffle Furnace (Arvinte et al., 2019). The ash percentage was calculated by the following formula:

$$C, \% = m_{CS} \cdot 100 / m_s$$

where m_s is sample mass before calcination, g; m_{CS} is sample mass after calcination, g.

Determination of mineral content

The mineral content was determined by using ICP – MS Agilent Technologies 7500 series spectrometer; the samples were digested with concentrated nitric acid and hydrochloric acid (Arvinte et al., 2019). The metal concentration (C) was expressed in mg/100 g of sample and was calculated by formula:

$$C = a \cdot V/m,$$

where a is standard concentration, mg/L; V is a volume of the acid that dissolves the sample, L; m is mineralized sample mass, g.

The mineral content was determined in *Vaccinium oxycoccus* fruits and in soil, taken from the area where the fruits were harvested.

Determination of nitrite content

The determination of nitrite content in small cranberries was made using Griess method (Neacsu and Chirigiu, 2006). In slightly acidic medium (acetic acid) the nitric acid (nitrite) mixed with sulfanilic acid and α -naphthylamine form a red nitric acid. The intensity of pink color of the nitric compound formed as a diazotizing reaction between sulfanilic acid and nitrites from deproteinized watery extract and the subsequent coupling with α -naphthylamine was measured. Also, the substance absorbance was measured at 520 nm wavelength versus a blank.

Determination of the antioxidant capacity

The determination of the antioxidant capacity was made through DPPH (2-diphenyl-1-picrylhydrazil), which is one of the most stable nitrogen alkyls and commercially available, with a maximum absorption UV-VIS at 517 nm. DPPH methanol solution has a maximum absorption at 517 nm wavelength, due to the unpaired electron. In the presence of an antioxidant, the electron pairs, resulting the simple form of DPPH-H, discolored, and the absorption disappears. The result of the decolorating is directly proportional with the number of the captured electrons, so inversely proportional with the absorbance. Determinations were made for watery extract: 5 g sample in 200 mL of water were boiled for 30 minutes and alcoholic extract: 1 g sample in 50 mL of ethanol, obtained on an ultrasound tub, at 40 °C and 25 KHz frequency from the plant berries. 5 mL of extract were mixed with 2.5 mL solution DPPH, $6 \cdot 10^{-5}$ M. Absorbance was determined on a fiber optic spectrophotometer from Ocean Optics, 5 min read time.

The inhibit percent of the free radicals, by comparison with DPPH was calculated with the formula:

$$I\% = A_0 - A_p/A_0 \times 100,$$

where A_0 is standard substance absorbance and A_p is analyzed sample absorbance (Paduret et al., 2016).

Determination of the total polyphenol content

The determination of the total content of polyphenols was made through Folin-Ciocalteu method, on the same extracts of 5 g samples in 200 mL water. Polyphenols are

substances with antioxidant specificity. They are aromatic chemical compounds with more hydroxyl groups inserted on aromatic ring. Due to this structure, they can be oxidized by Folin Ciocâlteu reagent (Fc), with the formation of blue coloration with maximum of absorption at 700 nm. Folin – Ciocâlteu indicator is specific only to the phenol compounds with reducing properties. The calibration curve was made using gallic acid solution (Su et al., 2007). The sample for analyses was made from 2 mL extract, 1 mL Folin Ciocâlteu reagent and 8 mL of 7.5% Na₂CO₃ solution, mixed for 5 minutes, left to still for 30 minutes in the dark and the reading of the sample absorbance was done at 750 nm (Sripakdee et al., 2015).

The result is expressed as Fc indicator, achieved by calculus formula:

$$Fc = A_{750} \cdot d \cdot 100$$

where A₇₅₀ is absorbance read at a 750 nm; d is sample dilution.

Identification and determination of the polyphenol content

Samples of 10 g of berries stepped into 100 mL of solvent (ethanol, ether and benzene) were analyzed. Phenolic extracts were analyzed using a liquid chromatography High Performance System (Shimadzu, Kyoto, Japan) equipped with liquid chromatograph LC-20 AD, auto sampler SIL-20A, column oven CTO-20AC and a detector with diode array SPD-M-20A. The separation was made on a Phenomenex Kinetex® 2,6 µm Bifenil 150 × 4,6 mm, column with 0,5 mL/min flow, and temperature controlled at 25°C. The sample injection volume was of 10 mL. A solvent system consisting of 0.1% acetic acid in water (A solvent) and acetonitrile (B solvent) was used with the following gradient: starting with 100% A and installing a gradient to obtain 5% B at 6.66 min, 40% B at 66.6 min and 80% B at 74 min, according to the method previously described with some modifications (Palacios et al., 2011). Solvent flow was of 1 mL/min. Phenol compounds were identified based on standard materials retention times and the quantification was made through chromatogram recording absorbance as oppose to external standards, at 280 nm for gallic acid, protocatechuic acid, vanillic acid, p-hydroxybenzoic acid and 320 nm for chlorogenic acid, caffeic acid, p-coumaric acid, rosmarinic acid, myricetin, quercetin, luteolin and kaempferol. All the standard calibration curves showed high linearity levels.

The analysis was done through infrared spectroscopy with Fourier transform (FT-IR) using a Nicolet i-20 spectrophotometer (ThermoScientific, SUA). The spectra were recorded in transmission mode using ATR system in the wave number range of 4000–400 cm⁻¹ at 4 cm⁻¹ resolution. SpectraGryph–spectroscopy software was used to display spectra. The samples (peatland cranberries extract in ethanol, ether and benzene) were placed on the ATR crystal and the spectra were recorded in triplicates.

Determination of vitamin C content

The samples were obtained through mixing 5 g grounded berries with 12 mL acid solution (10% perchloric acid and 1% o-phosphoric), completed with mono-potassium phosphate 0.02 mol/L. The samples were analyzed with HPLC Agilent Zorbax Extend- C18 columns, 5 µm particle size, I.D. × L 150 cm × 4.6 mm, flow rate was 1.0 mL/min.

Results and discussion

Chemical composition of cranberries

The moisture content of peatland cranberries was 84.1% (Table 1). This explains the fact that these plants grow only in swamp areas, with high humidity, as compared with blueberries (*Vaccinium myrtillus*) and lingonberries (*Vaccinium vitis-idea*), which grow in swamps along with peatland small cranberries, but also on alpine meadows and even in alpine forests. The results corroborate with other studies (Table 2), which identified moisture content from 84.2% up to 92% for small cranberries, the highest moisture content was detected in berries collected in spring, after the snow has melted (Česonienė et al., 2016).

Table 1
Content of moisture and ash in peatland small cranberries and the soil they grow on

| Sample | Ash (%) | Moisture (%) |
|------------------------------------|-------------------------|-------------------------|
| Peatland small cranberries berries | 1.38 ±0.09 ^b | 84.08±6.41 ^a |
| Peatland soil 1 | 12.53±0.90 ^a | 70.10±5.39 ^b |
| Peatland soil 2 | 12.51±0.99 ^a | 71.28±2.02 ^b |

For difference assessment was performed Student t-test. Values followed by a,b are statistically different at 95% confidence level.

Table 2
Comparison of the moisture and ash content in cranberries with those available in the literature

| Source | Content, % | |
|-------------------------|------------|-----------|
| | Moisture | Minerals |
| Our result | 84.1 | 1.38 |
| Česonienė et al. (2016) | 84.2–92.0 | 0.20–0.28 |

One can remark a strong correlation between the low minerals content in small cranberries and that of soil. However, the mineral content of small cranberries is much higher than the figures obtained in other studies (0.20–0.28%) (Česonienė et al., 2016).

Soil samples were taken from two distinct areas, as peat soil is heterogeneous. Regarding the ash content, the highest values were found in the soil, not in the fruit. The difference were not significant at $p < 0.05\%$. On the other hand, the moisture content was lower in the soil, differences being not significant at 95%

Most of the mineral elements found in the soil are also found in the cranberries fruit, but in smaller amounts (Table 3). There is an important calcium quantity in the studied peatland small cranberries, 11.04 mg/100 g, close to the average 13.0 mg/100 g related to other studies and significantly higher than the average calcium quantity from *Vaccinium macrocarpon*, 7.8 mg/100 g (Česonienė et al., 2016). Also, magnesium with 5.19 mg/100 g is situated between established limits by other studies, 2.9–9.1 mg/100 g. Manganese content of 0.05 mg/100 g is lower as opposed to other results 0.9–4.00 mg/100 g, although the manganese content in the soil is relatively high. Iron quantity of 0.23 mg/100 g is

significantly lower than the one reported, 0.11-0.42 mg/100g (Česonienė et al., 2016), but the majority is represented by iron divalent ion. Zinc quantity of 0.03 mg/100 g has lower values than in other determinations, 0.1 – 0,19 mg/100 g, as the copper quantity of 0.10 mg/100 g fits in other determinations limits, reaching the higher limit, 0.04 – 0.19 mg/100 g, and it is higher than in *Vaccinium macrocarpon*, 0.04 – 0.06 mg/100 g (Česonienė et al., 2016). Arsenic, mercury and antimony are below the approved limits and lead is under detection limits (Amariei et al., 2017). The difference in elements composition was significant (at 95% confidence level) for all the samples studied.

Table 3
Content of metals, mg/100 g, in peatland small cranberries and the soil they grow on

| Cranberries | | Soil 1 | Soil 2 | Cranberries | | Soil 1 | Soil 2 |
|-------------|-------------------------------|------------------------------|-------------------------------|-------------|------------------------------|--------------------------------|--------------------------------|
| Li | 0.09 ±0.0002 ^a | 0.02 ±0.0009 ^b | 0.006 ±0.0000 ^c | Zn | 0.03 ±0.0007 ^c | 0.02 ±0.0009 ^b | 0.04 ±0.0002 ^a |
| Na | 7.13 ±0.22 ^s | 1.60 ±0.10 ^c | 1.93 ±1.004 ^b | Mo | 2.95 ±0.12 ^c | 87.88 ±0.04 ^a | 86.59 ±4.20 ^b |
| Mg | 5.19 ±0.14 ^a | 1.89 ±0.11 ^b | 1.37 ±0.09 ^c | In | 0.02 ±0.0009 ^c | 0.05 ±0.002 ^b | 0.05 ±0.002 ^a |
| Al | 0.80 ±0.04 ^c | 14.43 ±0.50 ^b | 4.57 ±0.20 ^a | Sb | 3.72 ±0.12 ^c | 19.32 ±0.38 ^a | 16.72 ±0.35 ^b |
| Ca | 11.04 ±0.42 ^c | 109.53 ±2.30 ^a | 99.90 ±2.04 ^b | Cs | 0.22 ±0.011 ^c | 5.3673 ±0.1672 ^b | 5.7141 ±0.3974 ^a |
| Ti | 2.45 ±0.10 ^c | 44.90 ±3.28 ^b | 45.89 ±2.56 ^a | Ba | 0.20 ±0.009 ^c | 1.69 ±0.10 ^b | 1.77 ±0.10 ^a |
| V | 0.01 ±0.001 ^c | 1.66 ±0.10 ^a | 1.42 ±0.10 ^b | Pt | 0 ±0.0000 | undetectable | undetectable |
| Cr | 1.09 ±0.1 ^c | 11.71 ±0.53 ^b | 12.10 ±0.68 ^a | Au | 0 ±0.0000 | undetectable | undetectable |
| Mn | 0.05 ±0.003 ^c | 17.11 ±0.77 ^b | 17.59 ±0.77 ^a | Hg | 0.30 ±0.01 ^a | 0.01 ±0.0001 ^b | 0.01 ±0.0007 ^c |
| FeII | 0.22 ±0.001 ^c | 0.52 ±0.02 ^a | 0.48 ±0.01 ^b | Tl | 0.80 ±0.03 ^a | 0.03 ±0.0002 ^b | 0.03 ±0.0009 ^c |
| Fe III | 0.006 ±0.0005 ^c | 0.06 ±0.002 ^a | 0.04 ±0.004 ^b | Pb | 0 ±0.0000 | undetectable | undetectable |
| Cu | 0.10 ±0.009 ^c | 0.19 ±0.008 ^b | 0.39 ±0.002 ^a | | | | |

Superscript letters (a,b and c) refer to the comparison of the same element between the different samples; results followed by superscript letters are significantly different ($p < 0.05\%$) according to Turkey's post hoc test.

Comparison of the mineral content, mg/100 g, in peatland small cranberries with mineral content of the soil on which these berries grow is shown in Table 4.

Table 4
Comparison of the mineral content in peatland small cranberries, mg/100 g, with those available in the literature

| Minerals content | Our results, mg/100 g | Results available in the literature, mg/100 g | Reference |
|------------------|-----------------------|---|------------------------|
| Na | 7.13 | 2.00 | Nemzer et al., 2022 |
| Ca | 11.04 | 8.00–13.00 | Česonienė et al., 2016 |
| Mg | 5.19 | 2.9–9.1 | |
| Fe | 0.022 | 0.11–0.42 | |
| Mn | 0.048 | 0.90–4.00 | |
| Cu | 0.101 | 0.04–0.10 | |
| Zn | 0.019 | 0.10–0.19 | |

Determination of the antioxidant capacity and the total polyphenol content.

Antioxidant capacity and the polyphenol contents in peatland small cranberries are shown in Table 5.

Table 5
Antioxidant capacity and polyphenol content for the aqueous and ethanolic extract

| Parameter | Aqueous extract | Alcoholic extract |
|-----------------------------|--------------------------|--------------------------|
| Antioxidant capacity, I% | 60.40±2.00 ^a | 24.90±1.70 ^b |
| Polyphenol content, mg/100g | 340.78±2.33 ^a | 254.20±2.69 ^b |

It could be observed that the free radicals inhibition percentage was higher in aqueous extract. Wild cranberries antioxidant properties were compared with the grown cultivars, and a significantly higher antioxidant activity in wild cranberries was noticed (Borowska et al., 2009). Likewise, cranberries had a higher antioxidant potential than lingonberry, the adjacent plant from the peatland (Brown et al., 2012). One can observe that watery extract is richer in polyphenols than the alcoholic extract, the difference was significant $p < 0.05\%$.

By comparison (Table 6), other studies presented a polyphenol total content of 226.5 mg/100 g of fresh weigh (Narwojsz et al., 2019). Other authors determined a polyphenol total content, which varies from 288.5 to 456.3 mg/100 g (Borowska et al., 2009), up to 705 mg/100 g (Denev et al., 2013). One can notice a medium content in the studied berries. According to the results obtained by different authors, polyphenol total content is significantly higher in wild cranberries as opposed to grown varieties, 100.4 – 154.8 mg/100 g (Borowska et al., 2009)

Identification of polyphenols and determination of their content

Polyphenol content in extracts in ethanol, ether and benzene is shown in Table 7.

Table 6
Comparison of the antioxidant activity and total polyphenol contents in peatland small cranberries with those available in the literature

| Parameter | Extract | | Results available in the literature |
|------------------------------------|-----------|--------|---|
| | alcoholic | water | |
| Antioxidant capacity, I% | 24.9 | 60.2 | 87-96% (Kähkönen et al., 1999, 2001) 59-64% (Wang et al., 2000) 69.6% (Vattem et al., 2005) |
| Total polyphenols, mg/100 g | 254.20 | 340.78 | 705 (Denev et al., 2013) 288.5-456.3 (Borowska et al., 2009) 226.5 (Narwojsz et al. 2019) 347-389 (Česonienė et al., 2009) |

Table 7
Content of polyphenols in peatland small cranberries

| Polyphenolic compounds | Polyphenols content, mg/100 g product | | |
|------------------------|---------------------------------------|----------------------|-------------------------|
| | in ethanol | in ether | in benzene |
| λ=280 nm | | | |
| Gallic acid | 0±0.000 ^c | 0±0.000 ^c | 0±0.000 ^c |
| Protocatechuic acid | 0±0.000 ^c | 0±0.000 ^c | 0±0.000 ^c |
| 4-hydroxybenzoic acid | 0.41±0.02 ^a | 0±0.000 ^c | 0±0.000 ^c |
| Vanillic acid | 0±0.000 ^c | 0±0.000 ^c | 0±0.000 ^c |
| λ=320 nm | | | |
| Caffeic acid | 0±0.000 ^c | 0±0.000 ^c | 0±0.000 ^c |
| Chlorogenic acid | 0.42±0.02 ^a | 0±0.000 ^c | 0.01±0.01 ^b |
| P-coumaric acid | 0±0.000 ^c | 0±0.000 ^c | 0.27±0.001 ^a |
| Rosmarinic acid | 0.12±0.09 ^a | 0±0.000 ^c | 0±0.000 ^c |
| Myricetin | 0.23±0.01 ^a | 0±0.000 ^c | 0±0.000 ^c |
| Luteolin | 0±0.000 ^c | 0±0.000 ^c | 0±0.000 ^c |
| Quercetin | 0.39±0.01 ^a | 0±0.000 ^c | 0±0.000 ^c |
| Kaempferol | 0.07±0.003 ^a | 0±0.000 ^c | 0±0.000 ^c |
| Total | 1.630 | 0.000 | 0.371 |

When followed by different superscript letters (a, b, c), the values are statistically different at 95% confidence level.

One can see that the ethanolic extract is much richer in polyphenols than the ether and benzene extracts, excepting the P-coumaric acid, which appears in benzene extract (Table 8). It is obvious the p-hydroxybenzoic acid presence, as it appears in other research studies, its quantity value being very close to that found in large cranberry (*Vaccinium macrocarpon*) (Zuo et al., 2002). Likewise, one can observe the presence of the chlorogenic acid, p-coumaric acid (Jurikova et al., 2018, Zuo et al., 2002) as other researchers report, but also the rosmarinic acid which was not identified in other studies. All the difference found were not significant at 95% confidence level.

Table 8
Comparison of the polyphenols and vitamin C content, mg/100 g, in small cranberries with those available in the literature

| Polyphenol compound | Our results, mg/100 g | Results available in literature, mg/100 g | Reference |
|----------------------------|------------------------------|--|---|
| 4-hydroxybenzoic acid | 0.41 | N/A* | N/A |
| Caffeic acid | 0 | 0.7–1.4 | Jurikova et al., 2018, Zuo et al., 2002 |
| Chlorogenic acid | 0.42 | 61.0–96.3 | |
| P-coumaric acid | 0.27 | 2.0–78 | Jurikova et al., 2018, Zuo et al., 2002 |
| | | 2.02 | Ehala et al., 2005 |
| Rosmarinic acid | 0.12 | N/A | N/A |
| Myricetin | 0.23 | 8.4–11.2 | Chen et al., 2001 |
| Quercetin | 0.39 | 0.52–15.4 | Chen et al., 2001, Ehala et al. 2005 |
| Kaempferol | 0.07 | N/A | N/A |
| Vitamin C | 5.98 | 15.3–30 | Česonienė et al., 2016 |
| | | 14 | Nemzer et al., 2022 |
| | | 18 | Canja et al. 2016 |

Note: *N/A, not available.

As other authors show, the major flavonoids which appear in cranberries are quercetin and myricetin (Chen et al., 2001). The high content of quercetin, 5.15 mg/100 g of frozen weight, was reported (Ehala et al., 2005). Although the content found in the studied cranberries was lower, 0.39 mg/100 g, it is nevertheless a significant quantity. This substance contributes mainly in the antioxidant activity of the fruit. As for the quercetin content, the peatland cranberries are in the third place among the berries that contain this polyphenol, after elder and blueberries, and among vegetables only French and red onion have more quercetin than peatland cranberries (Kiviranta et al., 1988). There are multiple studies regarding this bitter-taste flavonoid, which has unique biological properties than can improve mental and physical performance and can reduce infection hazards. Quercetin stands out through anti-carcinogenic, anti-inflammatory, antiviral, antioxidant and psycho-stimulant activities and also through the capacity of lipid per-oxidation inhibition, platelet aggregation and mitochondrial biogenesis simulation (Li et al., 2016; MLcek et al., 2016). Quercetin may play an important role in treating several degenerative diseases (Palle et al., 2017; Pandey et al., 2012; Suganthy et al., 2016) without side effects or insignificant side effects. It was shown that quercetin and other flavonoids prevent the formation of atherosclerotic plaque, aggregation platelets (antithrombin effects) and favors the cardiovascular smooth muscles relaxation (Formica and Regelson, 1995). The quercetin antivirals' properties were investigated and proved on a large number of studies (Noor et al., 2021). As for myricetin content, cranberries are among the richest berries in this element (USDA, 2011). From the structural point of view, myricetin is similar to quercetin and it might have many of the latest functions (Ross et al., 2002). Studies show that myricetin has a therapeutic effect on many diseases (Song et al., 2021).

Vitamin C content

Vitamin C content in the studied berries (Table 8) was 5.98 mg/100 g, lower than the reported quantity in other studies, 15.3–30 mg/100 g (Česonienė et al., 2016), although the obtained results of vitamin C quantities in cranberries are quite different (Jurikova et al., 2018; Tikuma et al., 2014). It was shown that too ripened berries have a much lower vitamin C content, average 1.03 mg/100 g (Jurikova et al., 2018; Viskelis et al., 2009). Likewise, during storage a part of ascorbic acid transforms into its active biologic isomer, dehydroascorbic acid. Vitamin C content is positively correlated with antioxidant activity of these berries (Jurikova et al., 2018).

Conclusion

The obtained results show the antioxidant potential of peatland small cranberries and their possible usage in maintaining health, ageing and oxidative stress diminishing. It is known that quercetin and other polyphenols identified in peatland small cranberry have antioxidant, anti-inflammatory, vasodilatory, antithrombotic, antihypertensive, anticancer and probiotic properties (Lu et al., 2017), and this allows to recommend these cranberries for consumption as functional food.

Acknowledgements. The work was supported by the project "PROINVENT", Contract no. 62487/03.06.2022 – POCU/993/6/13 – Code 153299, financed by The Human Capital Operational Programme 2014–2020 (POCU), Romania.

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Application of milk protein concentrates in preparation of reduced fat sour cream

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Abstract

Keywords:

Sour cream
Fat
Protein
Whey
Caseinate
Microstructure

Introduction. It was shown the expediency of using protein-containing ingredients of dairy origin in the production of reduced fat sour cream.

Materials and methods. The fermentation kinetic of sour cream mixes was determined by the changes in titrated acidity. The microstructure of sour milk clots was studied using a light microscope. Rheological characteristics of reduced fat sour cream were determined using a rotational viscometry.

Results and discussion. The rational doses of milk-protein ingredients in reduced fat sour cream that prevent excessive acidity of milk cream during fermentation, structure and stabilize this product during 5 days of storage, are the following: skimmed milk powder, 1%, sodium caseinate, 0.5%, caseinate calcium, 0.75%, whey protein concentrate, 1%, hydrolyzed whey concentrate, 30%. According to the level of inhibition of the lactic acid fermentation, milk-protein concentrates in the specified quantities can be arranged in the following sequence: skimmed milk powder → whey protein concentrate → caseinate calcium → hydrolyzed whey concentrate → sodium caseinate.

By microstructural analysis of reduced fat sour cream, it was determined that 1% whey protein concentrate ensures proper moisture binding in the sour milk clot and contributes to the formation of a delicate structure with finely dispersed cells, while the use of 30% hydrolyzed whey concentrate forms a more viscous consistency of the product due to the presence of monosaccharides in it, which have a higher adsorption capacity for free moisture. The greatest structuring ability of caseinates and the most significant influence of whey proteins on the thixotropic properties of the reduced fat sour cream have been proved. A comprehensive indicator of the quality of reduced fat sour cream with milk-protein concentrates was calculated. Samples with 1% whey protein concentrate and 30% hydrolyzed whey concentrate had the most attractive sensory indicators, and got the highest score.

The chemical composition of reduced fat sour cream samples with whey proteins was studied. It was found that 1% of whey protein concentrate increases the biological value by 1.3%, while 30% of hydrolyzed whey concentrate decreases it by 3.5%. According to the research results, whey protein concentrate was classified as a biological enhancer with moderate technological properties, and hydrolyzed whey concentrate as an effective technological additive that imitates the quality indicators of an analogue with medium fat content of 18-20%.

Conclusions. The technological advantages of using whey concentrates in the composition of reduced fat sour cream as multifunctional ingredients have been shown.

Article history:

Received
10.04.2022
Received in
revised form
15.06.2022
Accepted
1.12.2022

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DOI:

10.24263/2304-
974X-2022-11-3-
8

Introduction

Sour cream is a sour milk product obtained by fermentation of milk cream, during which the process of lactic acid fermentation of milk sugar and coagulation of the casein fraction takes place, followed by the completion of structure formation during cooling and ripening at low temperatures (Chandan, 2015). Fat and milk proteins are mainly involved in the formation of the internal structure of sour cream (Narvhus et al., 2019). Thus, a high fat content provides an increase in the strength of the structure and viscosity of the finished product as a result of solidification and crystallization of milk cream (Buldo et al., 2013). That is why low-fat and reduced fat sour cream needs to rationalize its formulation in the absence of a sufficient amount of fat agglomerates, which are formed during the cooling of the sour milk clot and additionally stabilize its structure (Danylenko et al., 2020; Jervis et al., 2014).

According to the USDA Specifications for sour cream and acidified sour cream, sour cream with 10% of fat is a product that can be classified as "reduced fat" compared to its full-fat counterpart, which must contain at least 18% fat. At the same time, the Technical Regulations of the Customs Union (TR CU 033/2013) regulates the definition of sour cream as a product containing at least 10% milk fat. The release of low-fat and reduced fat types of sour cream is justified by the desire of manufacturers to meet the demand for low-calorie products, especially for people who follow a diet with a limited amount of saturated fat (Silva et al., 2020). However, various types of low-fat sour cream often have the defect of excessive acidity, which negatively affects the quality of the finished product (Fuquay et al., 2011). At the same time, scientists reported that milk protein concentrates in the composition of fermented milk products are able not only to effectively bind free moisture, but also to influence the activity of lactic acid microorganisms and, as a result, to regulate the product acidity during its production (Ağagündüz et al., 2021; Emkani et al., 2022). During production of sour cream with low content of protein or total solids, skimmed milk powder is usually added to the cream before fermentation, which has moderate techno-functional properties compared to highly purified milk protein concentrate (Christiansen et al., 2022; Crowley et al., 2016).

The use of whey proteins in the composition of a sour-milk dessert helps to obtain a delicate homogeneous consistency of the clot due to the high dispersion of micelles of whey proteins and the peculiarities of the gelation process (Izsó et al., 2020). In addition, whey proteins in a rational content prevent the syneresis of the clot, and are also one of the best fortifiers, which is related to their high biological value. At the same time, it is known that sodium, calcium, and ammonium caseinates have pronounced techno-functional properties (Abril et al., 2022; Mishyna et al., 2021), such as foam and gel formation, a high degree of free moisture binding (Khwaldia et al., 2004). Zhao et al. (2018) reported that 0.9% sodium caseinate in a whipped cream dessert leads to an increase in the density of the structure, viscosity of the consistency and is not inferior in its properties to whey proteins (O'Regan and Mulvihill, 2009). Li et al. (2020) proved that calcium caseinate increases the whipness of creamy desserts and stabilizes their structure, while sodium caseinate has a more moderate stabilizing ability. Another study indicated that potassium, sodium and ammonium caseinates are able to imitate the structure of full-fat analogues in imitation sour cream products or low-fat sour cream desserts (patent 3391002A US "Process for making imitation sour cream"). To achieve such an effect, their mass fraction should be at least 0.5%. However, it is known that caseinates, obtained by treating casein with alkalis, can significantly worsen the taste properties of food products, which makes it necessary to find their optimal doses (Polishchuk et al., 2020).

The use of liquid milk protein concentrate in the composition of reduced fat sour cream has not become widespread, which is due to the lack of scientific data on their techno-functional properties in the composition of the product, as well as their limited availability. It was reported about reduced fat sour cream, in the production of which it is allowed to use skimmed sweetened condensed milk, sodium caseinate from curd, prepared by wet heating method, liquid natural casein concentrate and others. At the same time, the authors of the article developed a method of obtaining liquid low-lactose whey concentrates (Osmak et al., 2021), which are appropriate for use in reduced fat products, which determines the scientific interest of this study.

The analysis of scientific and technical literature regarding the potential advantages of using milk protein concentrate in reduced fat sour cream technology makes it possible to single out the most technologically important of them:

- the possibility of preventing excessive acidity of milk cream during fermentation and storage of the finished product (Fuquay et al., 2011);
- formation of sensory indicators of reduced fat sour cream, similar to the full-fat product (Kew et al., 2020);
- the possibility of producing a dietary product of guaranteed quality with a mass fraction of fat 10% by a more progressive reservoir method (Osmak et al., 2021);
- improvement of consistency in terms of density, homogeneity, glossiness of the surface (Agarwal et al., 2015);
- the possibility of using completely natural ingredients of dairy origin (Early et al., 2012).

The aim of the work was to study the techno-functional properties of milk protein concentrate in the recipe composition of reduced fat sour cream with different amounts of their introduction.

To achieve the goal, the following tasks were defined:

1. To investigate the effect of milk protein concentrate in their variable amount on the activity of the development of lactic acid bacteria during the fermentation of cream mixes, and to choose a rational dose for each ingredient.
2. Determine the sensor and physicochemical indicators of reduced fat sour cream with the recommended content of milk protein concentrate.
3. To measure chemical composition of reduced fat sour cream samples with milk protein concentrate and calculate their biological value.

Materials and methods

Raw materials

For the production of reduced fat sour cream, milk cream with a fat content 10% was used. To normalize the mixes before fermentation, taking into account its dilution with protein-containing ingredients, cream with a fat content 20% was used.

The following milk-protein ingredients were selected: skimmed milk powder with a protein content 32%, sodium and calcium caseinates with a protein content 96%, whey protein concentrate obtained by ultrafiltration with a protein content 70%. Hydrolyzed whey concentrate with 40% of total solids (degree of lactose hydrolysis is 85%) was obtained by reconstitution in distilled water of demineralized dry sweet whey with a degree of demineralization 90% (content of ash no more than 2.5%, content of lactose no less than

79%, content of protein at least 10.7% in terms of total solids) according to the technology developed at the previous stage of scientific research (Osmak et al., 2021). To carry out the hydrolysis of whey concentrate with 40% of solids, the liquid preparation *β-D-galactosidase-hydrolase* "GODO-YNL2" ("Danisko", Denmark) with the recommended dosage at the level of 100 g of the preparation per 100 l of milk and single-strain lyophilized starter culture "*L. acidophilus* LYO 50 DCU-S" ("Danisko", Denmark) at the recommended dose of 5 g of the drug per 100 liters of milk were used.

A starter culture with the following composition was selected for the fermentation of milk cream: *Lactococcus lactis*, *L. cremoris*, *L. diacetylactis*, and *Streptococcus thermophilus*. This composition of lactic acid microorganisms ensures the intensification of the lactic acid fermentation process. The manufacturer's recommended amount of the preparation is 0.5 g per 1 liter. Before adding to the cream mix, the starter culture was activated in a nutrient medium. With a scalpel, heated over an open fire, the lyophilized starter was weighed and added to the pre-calculated amount of milk, which was pasteurized at a temperature of 84–88 °C with a duration of 3–5 min and cooled to a fermentation temperature of 28–32 °C. The duration of fermentation was an average of 6–8 hours until the titrated acidity of 60 °T was reached.

Preparation of samples

Samples of reduced fat sour cream contained:

- 10% milk fat, which makes it possible to classify this type of product as reduced fat;
- not less than 17.3% of total solids, which ensures the formation of the proper structure of the product;
- not less than 2.6% of protein, which corresponds to the well-known recommendations for the production of sour cream.

For the production of reduced fat sour cream samples, milk protein concentrate was dissolved directly in cream with a fat content 10% at a hydromodule of 1:10 and a temperature of 40 °C with a duration for 30–40 min for preliminary swelling, followed by heat treatment at a temperature of 85–90 °C for 2–3 min to ensure microbiological purity and effective dissolution of protein ingredients.

Milk protein concentrate mixes were filtered, cooled and added during mixing to milk cream that was pasteurized at temperatures of 85–90 °C with a duration of 15–20 s, followed by cooling to the fermentation temperature and normalization with cream with a fat content of 20%, after which the mix was fermented. During the first three hours, the cream mix was thoroughly stirred every hour and then left until the end of fermentation process.

Fermentation of cream mixes was carried out at a temperature of 28–32 °C for 4–12 h until the titrated acidity of 60–75 °T was reached, followed by cooling and ripening at a temperature of 4–8 °C for 6–8 h. Experimental samples of reduced fat sour cream were stored for 5 days.

Research methods

Titrated acidity. The titrated acidity of the clots during fermentation, after ripening and during storage was determined using a method (Tomovska et al., 2016).

Syneresis of sour milk clots. Syneresis of sour milk clots was determined by the centrifugal method. The same amount of product was weighed into two glass tubes with a

capacity of 10 cm³, closed with stoppers and centrifuged for 10 min at a speed of 1000 min⁻¹. The layer of whey, that settled on top of the sample, was determined on a scale in cm³.

Microstructure of sour milk clots. The microstructure of sour milk clots was studied by microscopy of preparations using a light microscope at a magnification of 10×15. A clot sample was taken and covered with a cover glass. Photomicrographs were obtained using an Olympus CX 41 light microscope and a digital camera.

Fat content. The mass fraction of fat was determined by the acid method, which is based on the separation of fat under the action of sulfuric acid and isoamyl alcohol, followed by centrifugation and calculation.

Protein content. The mass fraction of protein in reduced fat sour cream sampled with milk protein concentrate was determined by the Kjeldahl method.

Total content of solids. The determination of the mass fraction of solids in reduced fat sour cream with milk protein concentrate was carried out using a drying cabinet according to the traditional method proposed by the Association of Official Analytical Chemists (2016) and the methodology defined by the Adolfo Lutz Institute (Zenebon and Pascuet, 2005).

Viscosity-speed characteristics. The effective viscosity of reduced fat sour cream samples was determined on a rotary viscometer with a "cylinder-cylinder" system by measuring the kinetics of deformation. Shear stress τ (Pa) was measured at a temperature of 20 °C at twelve values of the shear rate gradient (γ) in the range from 3 to 1312.2 s⁻¹ during forward and reverse motion (Bass et al., 2017). The maximum effective viscosity of an almost undamaged structure ($\gamma = 3 \text{ s}^{-1}$), the minimum effective viscosity of an extremely damaged structure ($\gamma = 1312.2 \text{ s}^{-1}$) and the effective viscosity of a restored structure ($\gamma = 3 \text{ s}^{-1}$) were determined. The thixotropic ability of the test samples was determined as a percentage by the difference in the values of the effective viscosity of the practically intact structure at the beginning and at the end of the measurement at a shear rate gradient ($\gamma = 3 \text{ s}^{-1}$).

Comprehensive quality indicator. The overall comprehensive quality indicator (K) of the samples was determined as a set of the following characteristics: nutritional value (K₁), sensory indicators (K₂), viscosity-speed characteristics (K₃).

The overall comprehensive quality indicator was determined according to the equation:

$$K = K_1 \times M_1 + K_2 \times M_2 + K_3 \times M_3,$$

where K is a general complex indicator;

M_{1, 2, 3} are coefficients of importance for each of the groups of indicators K_{1, 2, 3}.

Biological value. The amino acid composition of experimental samples of reduced fat sour cream was determined by a special method (Bobel et al., 2022). Based on the obtained values, the amino acid score was calculated, which is the ratio of the content of the essential amino acid product to the content of the corresponding essential amino acid of the "ideal protein" according to the FAO/WHO scale (Kowalczewski et al., 2019). The coefficient of difference of amino acid score and biological value was calculated according to the method of M. M. Chernikov.

Statistical processing. The obtained results were calculated and graphically displayed using the standard program Microsoft Office Excel 2016. The accuracy of the obtained results was ensured by threefold repetition of the experiment.

Results and discussion

Effect of milk protein concentrate on the fermentation process of sour milk mixes

The viscosity and consistency of sour cream depend on the chemical composition and efficiency of the fermentation process. As a result of coagulation of the protein fraction of casein, a milk clot is formed and the high-melting glycerides of fat globules solidify, which affects the reduction of the negative charge of fat globules and the formation of "fat clusters" (Jollès, 1975). Fat globules are part of protein molecules and gradually form connecting bridges with them (Farrell et al., 2006), which ensures the formation of a stronger milk clot. In low-fat or reduced fat sour cream, due to the small number of fat balls, a liquid consistency is formed. As a result, milk clot is not dense and has a high degree of syneresis. The milk clot can reach the highest density at the isoelectric point of plasma proteins and fat globule shells (4.6–4.7 pH) (Bozoglu and Erkmen, 2016), which confirms the need to end the fermentation process when the titrated acidity values are reached at the level of 60–75 °T with taking into account the fact that during the slow cooling of the clot, partial ripening of sour cream occurs.

The use of milk proteins in the formulation of reduced fat sour cream slows down the process of moisture separation due to its effective binding during hydration, which can somewhat inhibit the development of lactic acid microflora during fermentation (Lucey, 2002). Considering, that the production of reduced fat sour cream is often associated with the formation of excessive acidity, this property of milk proteins can help in its regulation. However, in the scientific literature there is a lack of data on the fermentation process of milk mixes in the presence of milk protein concentrate. That is why it was decided to investigate in more detail way the dependence of the change in the titrated acidity of sour milk mixes with different milk protein concentrate at a variable amount during fermentation for 12 hours. The dosage ranges for each of the milk protein concentrate were as follows: skimmed milk powder, 1–2%, sodium caseinate, 0.5–1%, calcium caseinate, 0.5–1%, whey protein concentrate, 0.5–1%, hydrolyzed whey concentrate, 20–40%. The selection of the indicated ranges is due to the generally accepted recommendations for the use of the selected concentrates and ensuring the protein content in quantities of at least 3%. Thus, the mass fraction of milk proteins in the selected ranges of milk protein concentrate content was: skimmed milk powder, 3–3.29%, sodium caseinate and caseinate calcium, 3.16–3.64%, whey protein concentrate, 3.03–3.38%, hydrolyzed whey concentrate, 3.04–3.37%.

Data on the study of the fermentation kinetics of sour milk mixes are given in Table 1.

It can be concluded that in the presence of 1–1.5% of skimmed milk powder lactic acid microflora is quite active, as evidenced by the achievement of the recommended values of titrated acidity already at the 6th hour of fermentation (Table 1). With a further increase in the dosage of skimmed milk powder, the process of lactic acid fermentation is significantly activated, which is evidenced by the excess of the recommended values of titrated acidity at the indicated moment of fermentation. This effect can be explained by the presence of skimmed milk powder in the product as a source of lactose and minerals, which are a nutrient medium for microorganisms of the starter culture and stimulate their development (Lante et al., 2006).

Despite the fact that skimmed milk powder is one of the cheapest and most accessible types of protein-containing dairy ingredients, its use will not prevent significantly excessive acidity. Instead, the introduction of such protein ingredients as sodium caseinate, caseinate calcium, whey protein concentrate into the composition of sour milk mixes inhibits the process of lactic acid fermentation, which is mainly due to their ability to actively bind free moisture.

Table 1
Titrated acidity of sour milk mixes during fermentation at different doses of protein concentrates, °T, (P ≥ 0.95; n = 3)*

| Mass fraction of milk protein concentrate, % | Duration of fermentation, hours | | | | |
|--|---------------------------------|----|----|----|-----|
| | 4 | 6 | 8 | 10 | 12 |
| Sour cream | | | | | |
| - | 43 | 74 | 86 | 92 | 97 |
| Sour cream with skimmed milk powder | | | | | |
| 1.0 | 42 | 72 | 86 | 92 | 96 |
| 1.5 | 44.5 | 75 | 89 | 93 | 99 |
| 2.0 | 46 | 79 | 92 | 98 | 103 |
| Sour cream with sodium caseinate | | | | | |
| 0.5 | 37 | 67 | 74 | 87 | 91 |
| 0.75 | 31 | 49 | 64 | 75 | 81 |
| 1 | 30 | 44 | 56 | 67 | 74 |
| Sour cream with caseinate calcium | | | | | |
| 0.5 | 37 | 71 | 83 | 88 | 93 |
| 0.75 | 34 | 65 | 75 | 83 | 88 |
| 1 | 32 | 58 | 68 | 74 | 79 |
| Sour cream with whey protein concentrate | | | | | |
| 0.5 | 36 | 65 | 80 | 87 | 90 |
| 0.75 | 35 | 64 | 75 | 84 | 87 |
| 1.0 | 30 | 59 | 69 | 78 | 82 |
| Sour cream with hydrolyzed whey concentrate | | | | | |
| 20 | 37 | 65 | 78 | 84 | 87 |
| 30 | 33 | 58 | 70 | 79 | 84 |
| 40 | 27 | 51 | 59 | 65 | 71 |

* Note: titrated acidity values corresponding to the recommended acidity range (60–75 °T) for sour cream with 10% of fat are highlighted with a gray background

The use of hydrolyzed whey concentrate significantly increases the total solids. As a result, with an increase in the dose of milk protein concentrate, the osmotic pressure increases, which suppresses the development of lactic acid microorganisms. According to the degree of inhibition of the process of lactic acid fermentation, milk protein concentrate can be arranged in the following sequence according to the degree of growth: 1% skimmed milk powder → 1% whey protein concentrate → 0.75% caseinate calcium → 30% hydrolyzed whey concentrate → 0.5% sodium caseinate. Despite the higher protein content in hydrolyzed whey concentrate, compared to other protein ingredients, it inhibits the fermentation process less actively than sodium caseinate at a lower dose, which can be justified by the presence of lactose hydrolysis products in it, namely the monosugars – glucose and galactose. It is known that they are a nutrient medium for lactic acid microorganisms and stimulate their development more actively than the presence of milk sugar (Sharma et al., 2017).

A similar dynamic of partial inhibition of the fermentation process of the sour milk mix using liquid whey-based concentrates was also noted in the study of yogurt mixtures (Wherry et al., 2019). However, during 6–6.5 hours of fermentation, the acidity reached 80–85 °T, which is much higher than the obtained results and is a consequence of the use of acid whey instead of sweet. According to well-known recommendations for the production of reduced sour cream, the fermentation process should last at least 6 hours until the titrated acidity value of 60–75 °T is reached (Anderegg et al., 1929). Its further growth to the value of the isoelectric point of casein can lead to the restart of the protein fraction and, as a result, the destruction of energy bonds, the loss of thixotropic ability and the formation of a loose clot consistency. For further research, the optimal dosage for each of the milk protein concentrate was chosen based on the data on the dependence of the fermentation of the sour milk mix on the amount of the protein ingredient, which aimed to ensure a proper correlation between the desire to achieve the set technological effect and simultaneously increase the biological value of the finished product. For skimmed milk powder, a mass fraction of 1% was determined as the one that does not contribute to the intensification of the lactic acid fermentation process. For sodium caseinate and caseinate calcium their ability to negatively affect organoleptic indicators, namely to worsen the taste of the finished product, which is associated with the technology of obtaining caseinates from the use of alkalis, was additionally taken into account. Sodium caseinate has a more pronounced alkaline-bitter taste than caseinate calcium, so its maximum dose should not exceed 0.75% of the composition of dairy products (Polishchuk et al., 2021). Considering the fact that sodium caseinate inhibits the process of development of microorganisms to a greater extent than caseinate calcium, its dose was chosen at the level of 0.5%, and caseinate calcium, 0.75%. The mass fraction of whey protein concentrate as the one that least inhibits the development of lactic acid microorganisms, was chosen at the level of 1%. For hydrolyzed whey concentrate, the optimal amount was set at the level of 30%. Increasing the dose to 40% makes it possible to reach the recommended value of titrated acidity only during 12 hours of fermentation, which is impractical from an economic point of view.

Quality indicators of reduced fat sour cream with different amounts of milk protein concentrate

The consistency of reduced fat sour cream with an increase in the content of total solids improves due to the increase in viscosity and the formation of a dense structure. In order to verify this statement, the microstructure of the sour cream clots with milk protein concentrate was investigated (Figure 1).

A sample of reduced fat sour cream with 1% whey protein concentrate is the most homogeneous (Figure 1), which causes maximum moisture retention. The sour cream with 0.75% caseinate calcium is characterized by a lower ability to form a homogeneous clot (Figure 1), which is associated with its high gel-forming properties, as a result of which it forms a fairly dense gel network with larger cells, compared to the sample with whey protein concentrate. At the same time, 0.5% sodium caseinate exerts a more moderate synergistic effect on the structure of the sour milk clot due to the formation of cells of slightly different sizes with a lower density of the structure than in the case of using caseinate calcium. The addition of 1% skimmed milk powder slightly reduces the size of cells with a moisture in clot compared to the control, but this dose is not sufficient to prevent syneresis. At the same time, an increase in the content of skimmed milk powder in the reduced fat sour cream can lead to an increase of acidity.

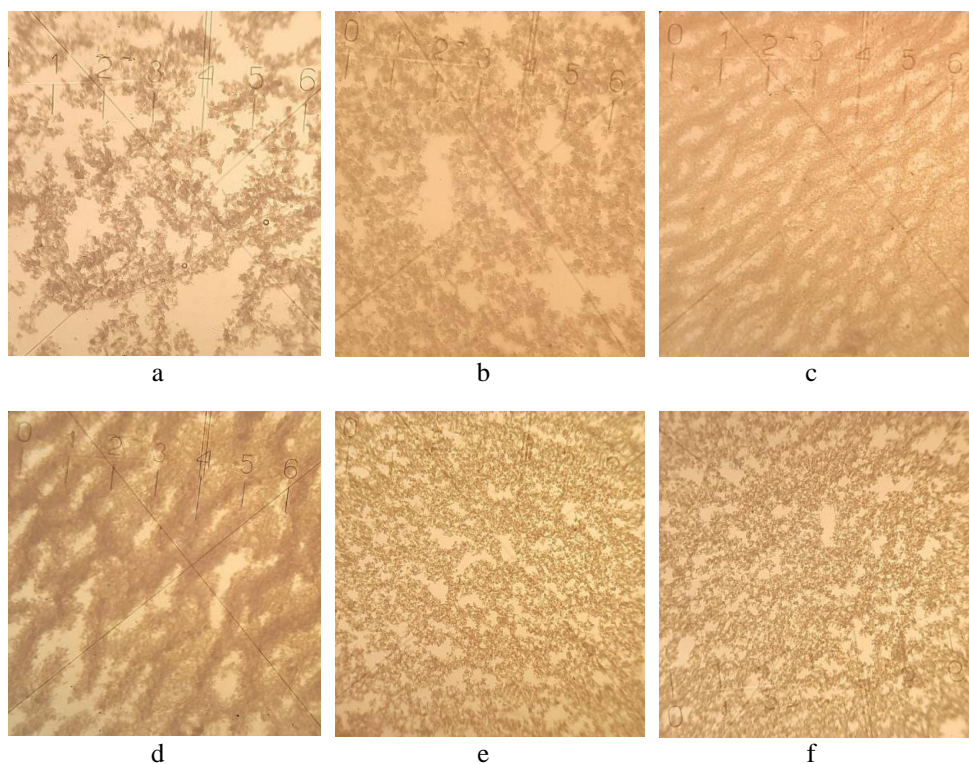


Figure 1. Microstructure of reduced fat sour cream with and without milk protein concentrate: a, control; b, 1% skimmed milk powder; c, 0.5% sodium caseinate; d, 0.75% caseinate calcium; e, 1% whey protein concentrate; f, 30% hydrolyzed whey concentrate.

The use of 30% hydrolyzed whey concentrate, despite the high content of solids, in particular protein, leads to the formation of a homogeneous and viscous consistency. Hydrolyzed whey concentrate is somewhat inferior to whey protein concentrate and caseinate calcium in terms of the dispersion of free moisture and its distribution in the clot, but it is able to form a more delicate, cream-like structure of the product, unlike sodium caseinate and caseinate calcium. Augustin et al. (2003) obtained yogurt with an improved consistency because of the use of whey protein concentrate (25–56% protein), the clot of which had a low level of whey separation. At the same time, the use of whey protein concentrate with a high protein concentration (63–64%) did not always have a positive effect on the sour milk clot, which differs from the results obtained in this study and can be explained by the specific interaction of proteins and fat globules at their high concentration, in compared to low-fat yogurt.

Sour milk clot with hydrolyzed whey concentrate is less liquid than clot with whey protein concentrate, which can be explained by the presence in it of monosugars – glucose and galactose, which have an increased degree of adsorption of free moisture (Qi and Tester, 2019), but this information requires additional research.

For this purpose, the effective viscosity of the studied samples of reduced fat sour cream with different milk protein concentrate was investigated. The viscosity-speed characteristics of sour cream clots with different milk protein concentrate in recommended quantities are shown in Table 2.

Table 2
Viscosity-speed characteristics of reduced fat sour cream with different milk protein concentrates ($P \geq 0.95$, $n = 3$)

| Type of milk protein concentrate in reduced fat sour cream | Effective viscosity (mPa·s) under variable shear rate gradient | | | The time of ultimate destruction of the structure ($\gamma = 1312.2 \text{ c}^{-1}$), min | The degree of structure recovery, % |
|--|--|----------------------------------|---------------------------------------|---|-------------------------------------|
| | $\gamma = 3 \text{ c}^{-1}$ (straight) | $\gamma = 1312.2 \text{ c}^{-1}$ | $\gamma = 3 \text{ c}^{-1}$ (reverse) | | |
| 1 | 2 | 3 | 4 | 5 | 6 |
| control | 210.2±11.6 | 15.0±1.1 | 80.2±9.1 | 2.0±0.1 | 38.2 |
| 1% SMP | 298.4±12.5 | 20.1±1.0 | 120.3±5.2 | 3.2±0.2 | 40.3 |
| 0.5% SC | 329.1±10.4 | 25.5±1.5 | 156.1±11.0 | 6.0±0.3 | 47.4 |
| 0.75% CC | 313.4±14.5 | 24.8±1.1 | 142.7±9.2 | 7.0±0.2 | 45.5 |
| 1% WPC | 289.2±11.3 | 18.7±0.9 | 148.3±5.5 | 5.4±0.1 | 51.3 |
| 30% HWC | 298.0±10.9 | 19.8±1.0 | 157.8±6.8 | 5.8±0.2 | 52.9 |

Note: MPC, milk protein concentrate; SMP, skimmed milk powder; SC, sodium caseinate; CC, caseinate calcium; WPC, whey protein concentrate; HWC, hydrolyzed whey concentrate.

The available milk proteins in reduced fat sour cream without milk protein concentrate (control) do not provide proper structuring and high thixotropy ability of sour cream clot (Table 2). Skimmed milk powder slightly increases structuring in reduced fat sour cream, but the ability to recover increases insignificantly, compared to the control sample. Milk protein concentrate based on whey proteins (whey protein concentrate, hydrolyzed whey concentrate) show a structuring ability at the level of skimmed milk powder, but the thixotropy of the structure of destroyed clots with these concentrates is the largest among all the studied samples and reaches values of 51.3–52.9%. This property is very important in the technology of sour cream and sour cream analogues, because when they are pumped into the hopper of the packaging machine with the help of a pump, clot of low-fat or reduces fat sour cream are usually partially or irreversibly destroyed. This leads to the loss of consumer properties characteristic of the product. Danylenko et al. (2020) reported the ability of reduced fat sour cream (10–15% fat) to show thixotropy, however, in the presence of hydrocolloids, but it is significantly less than in presence of milk protein concentrate. In addition, to establish the necessary viscosity indicators, the fermentation process should last at least 8–9 hours instead of 6 hours.

Sodium caseinate and caseinate calcium have the highest structuring ability due to their specific gel-forming ability (Table 2). At the same time, thixotropic properties of samples with caseinates occupy an intermediate place between skimmed milk powder, whey protein concentrate, and hydrolyzed whey concentrate. The highest thixotropy of samples with whey protein concentrate and hydrolyzed whey concentrate can be explained by their specific ability to evenly distribute fat and free moisture in protein matrices (Relkin et al., 2006), which contributes to the formation of more contacts between protein macromolecules and, accordingly, increases the ability to restore of sour milk clots. In the case of sodium caseinate and caseinate calcium, the formation of a dense structure with an uneven distribution of components in the spatial matrix of the product somewhat reduces the ability to self-restore the structure of destroyed clots, compared to milk protein concentrate based on whey proteins. Patterns of structuring of samples with different milk protein concentrate are also

confirmed by the different time of ultimate destruction of the structure at the maximum shear rate gradient, which is minimal for the control sample and maximal for samples with caseinates.

At the next stage, the dynamic of changes in titrated acidity and the degree of syneresis of reduced fat sour cream with milk protein concentrate during 5 days of storage was studied. The highest acidity was observed when using 1% skimmed milk powder, which during 5 days of storage reached 101 °T. Such result is a defect of excessive acidity. The application of 1% whey protein concentrate is characterized by a stable increase in acidity throughout the entire storage period, while for 0.75% sodium caseinate and 0.5% caseinate calcium, after the 3rd day of storage, a slowdown in titrated acidity growth is observed. The lowest acidity was established for sour cream with 30% hydrolyzed whey concentrate, which steadily increased to 88 °T. Inhibition of the process of increasing acidity in samples with sodium caseinate, caseinate calcium, and hydrolyzed whey concentrate during storage is a consequence of the increased protein content, which affects the reduction of lactic acid production, as a result of which the concentration of hydrogen ions increases (Wherry et al., 2019). The degree of syneresis of reduced fat sour cream with milk protein concentrate for all samples increased during the storage period (Figure 2).

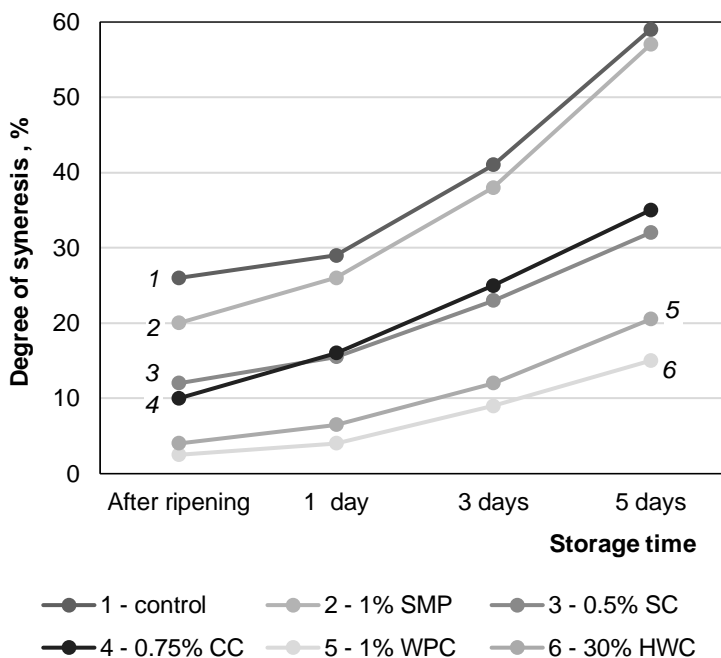


Figure 2. Degree of syneresis of reduced fat sour cream samples during 5 days of storage, % ($P \geq 0.95$, $n = 3$). SMP, skimmed milk powder; SC, sodium caseinate; CC, caseinate calcium; WPC, whey protein concentrate; HWC, hydrolyzed whey concentrate.

The highest value (59%) was recorded for the control sample at the end of the storage period. The addition of 1% skimmed milk powder slightly reduced the whey separation after production, but later the syneresis value approached the control sample. It is interesting that for the sample with 0.75% caseinate calcium, the degree of syneresis after sour cream ripening was lower than for the sample with 0.5% sodium caseinate. After the 1st day of storage, this indicator became higher for the sample with caseinate calcium, which can be

justified by the presence of large cells with free moisture, which was confirmed by the results of the microstructure analysis of the sample with 0.75% sodium caseinate. The greatest retention of whey was provided by 1% whey protein concentrate (degree of syneresis on the 5th day – 15%) due to the finely dispersed distribution of moisture in the product. For 30% hydrolyzed whey concentrate, this indicator was slightly higher than whey protein concentrate, and during storage, this difference increased insignificantly. The decrease in the degree of syneresis in test samples with milk protein concentrate also occurs due to the increased moisture-binding capacity of protein ingredients, which for milk protein concentrate based on whey proteins is significantly higher than other protein ingredients (Akalin et al., 2012; Tirado et al., 2007).

It was established that the use of protein concentrates (whey protein concentrate, caseinate calcium, sodium caseinate, hydrolyzed whey concentrate) in reduced fat sour cream helps not only to regulate the increase in acidity during lactic acid fermentation, but also during the storage period up to 5 days.

Physicochemical indicators of test samples are given in Table 3.

Table 3
Physicochemical indicators of reduced fat sour cream with milk protein concentrates
($P \geq 0.95$; $n = 3$)

| Indicator | Samples | | | | | |
|--------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | Control | 1% SMP | 0.5% SC | 0.75% CC | 1% WPC | 30% HWC |
| Total content of solids, %, not less | 16.9 ±0.1 | 18.5 ±0.0 | 18.1 ±0.1 | 18.3 ±0.0 | 18.4 ±0.0 | 27.8 ±0.0 |
| Protein content, %, not less | 2.6 ±0.0 | 3.0 ±0.1 | 3.2 ±0.0 | 3.4 ±0.0 | 3.4 ±0.0 | 3.2 ±0.0 |
| Fat content, %, no less | 10.1±0.0 | | | | | |

Note: SMP, skimmed milk powder; SC, sodium caseinate; CC, caseinate calcium; WPC, whey protein concentrate; HWC, hydrolyzed whey concentrate.

Protein content is the largest in samples of reduced fat sour cream with caseinate calcium, whey protein concentrate, and hydrolyzed whey concentrate. Taking into account the high percentage of use of hydrolyzed whey concentrate (30%) in the reduced fat sour cream recipe, compared to other milk protein concentrate, the sample with it has the highest solids content (27.8%), which at this level corresponds to the indicator of sour cream with a mass fraction of fat 18–20%. Due to use of hydrolyzed whey concentrate it is possible to obtain a reduced fat product, which is an analogue of a full-fat product according to certain physicochemical parameters. The use of 1% skimmed milk powder makes it possible to obtain a product with a higher content of solids than in traditional sour cream with 10% of fat with a large proportion of carbohydrates in its composition. The content of total solids in samples with whey protein concentrate, caseinate calcium, and sodium caseinate is somewhat lower, although it is within the recommended range of values.

In order to evaluate the effect of milk protein concentrate on the characteristics of reduced fat sour cream, the nutritional value was calculated, a sensory evaluation was carried out and the results of the rheological indicators were taken into account, based on the results of which a comprehensive quality indicator was calculated (Table 4).

Table 4

Comprehensive indicator of the quality of reduced fat sour cream product samples, points

| Indicator | Coefficients of importance | Samples | | | | | |
|---------------------------------|----------------------------|---------|--------|---------|----------|--------|---------|
| | | Control | 1% SMP | 0.5% SC | 0.75% CC | 1% WPC | 30% HWC |
| Nutritional value | 0.3 | 1.0 | 1.04 | 1.03 | 1.04 | 1.05 | 2.09 |
| Sensory indicators | 0.4 | 0.62 | 0.7 | 0.78 | 0.73 | 0.98 | 0.9 |
| Viscosity-speed characteristics | 0.3 | 1.0 | 1.28 | 2.12 | 2.35 | 2.03 | 2.14 |
| Comprehensive assessment (K) | | 0.85 | 0.97 | 1.26 | 1.31 | 1.38 | 1.87 |

Note: SMP, skimmed milk powder; SC, sodium caseinate; CC, caseinate calcium; WPC, whey protein concentrate; HWC, hydrolyzed whey concentrate.

Reduced fat sour cream with 30% hydrolyzed whey concentrate and 1% whey protein concentrate received the highest number of points. At the same time, it was found that whey protein concentrate gives the product an astringent aftertaste, which is caused by the whey protein extraction technology (Childa and Drake, 2010). In contrast, hydrolyzed whey concentrate gave the product a sweet aftertaste, which is justified by the higher degree of sweetness of glucose and galactose in its composition (Helstad, 2019). In addition, the use of both whey protein concentrate and hydrolyzed whey concentrate gives the product a yellowish tint, which is due to the chemical properties of the whey.

An important indicator of the quality of reduced fat sour cream is the milky or creamy taste (Jervis et al., 2014), which was noted for the use of milk protein concentrate based on whey proteins, because they have ability to mimic milk fat. Sodium caseinate, even at a reduced dose of 0.5%, somewhat gives a slight bitter aftertaste, while caseinate calcium excessively thickens the product to the formation of an overly dense structure. The nutritional value of the sour cream product increases by 1.03–1.05 times and by 2.09 time for the sample with hydrolyzed whey concentrate, which is due to the high content of carbohydrates and protein in its chemical composition.

Biological value of reduced fat sour cream with milk protein concentrates

According to the results of the comparison of quality indicators, samples of reduced fat sour cream with 1% whey protein concentrate and 30% hydrolyzed whey concentrate were selected for further investigation of their biological value, as those that differ in high protein content and have the most attractive taste qualities for the consumers. In order to determine the biological value of the developed compositions of reduced fat sour cream, the content of amino acids in 3 samples was determined: control, 1% whey protein concentrate, 30% hydrolyzed whey concentrate. The calculation of the amino acid score of essential amino acids was carried out and then their content was compared to the reference values of the FAO/WHO (Table 5).

It can be concluded that the limiting amino acid in all experimental samples is valine (Table 5). However, the score value for each of the essential amino acids does not provide a complete understanding of the biological value of the finished product, so the coefficient of difference of amino acid score (CDAAS) was calculated according to the method of M. P. Chernikov (Figure 3).

Table 5

Amino acid score of experimental samples, %

| Amino acid | FAO/WHO standard, g/100g of "ideal protein" | Amino acid score, % | | |
|--------------------------|---|---------------------|--------|---------|
| | | Control | 1% WPC | 30% HWC |
| lysine | 5.5 | 78.2 | 79.8 | 74.6 |
| threonine | 4.0 | 62.5 | 63.8 | 64.8 |
| methionine + cystine | 3.5 | 97.1 | 98.6 | 92,7 |
| valine | 5.0 | 52.0 | 53.1 | 50.1 |
| isoleucine | 4.0 | 52.5 | 54.0 | 51.8 |
| leucine | 7.0 | 68.6 | 70.5 | 66.0 |
| Phenylalanine + tyrosine | 6.0 | 76.7 | 77.9 | 64.7 |

Note: WPC, whey protein concentrate; HWC, hydrolyzed whey concentrate.

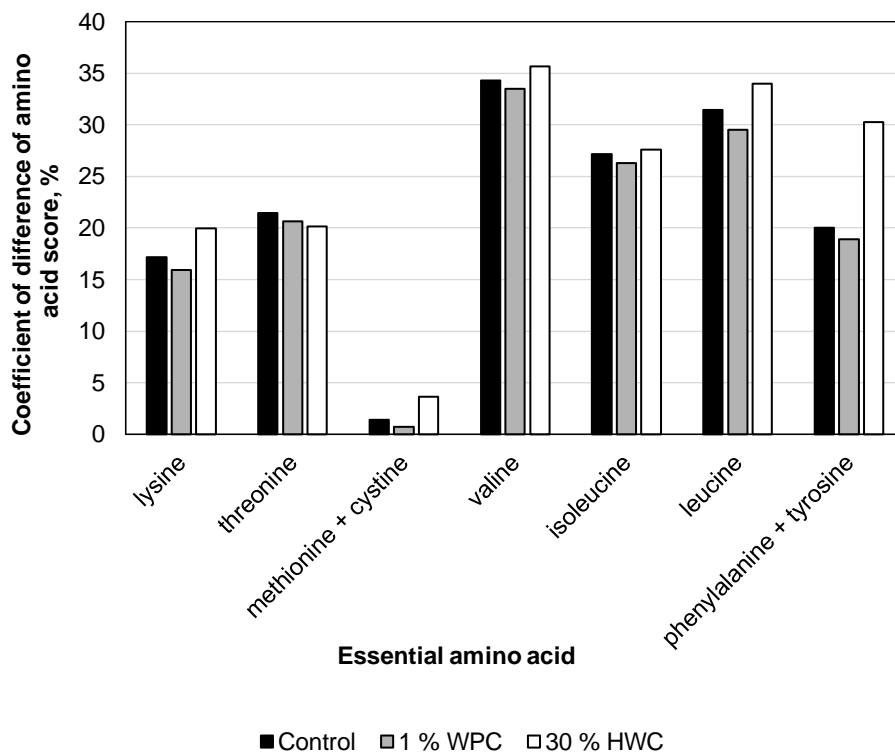


Figure 3. Coefficient of difference of amino acid score in experimental samples, %. WPC, whey protein concentrate; HWC, hydrolyzed whey concentrate.

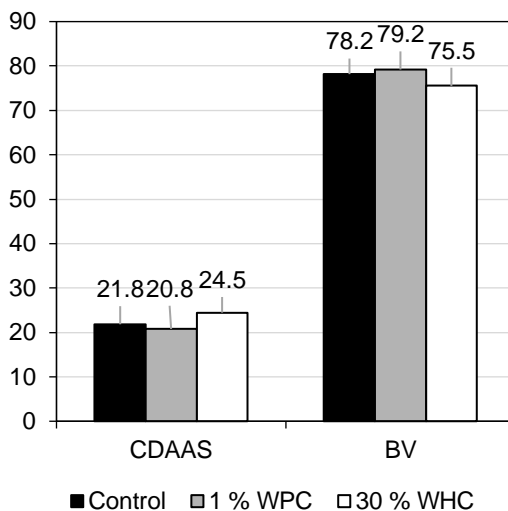


Figure 4. Biological value of reduced fat sour cream, %. WPC, whey protein concentrate; WHC, hydrolyzed whey concentrate.

The maximum excess for all samples is provided by valine (Figure 3). Thus, the smaller the value of the CDAAS, the more fully the essential amino acid is used for the needs of biosynthesis, which is shown in Figure 4.

For control sample the biological value is 78.2% (Figure 4). Addition of 1% whey protein concentrate leads to its increase by 1.3%, while the use of 30% of hydrolyzed whey concentrate reduces it by 3.5%. This trend can be explained by the fact that the percentage of substitution of milk cream, which is a source of high-quality protein, with hydrolyzed whey concentrate in the recipe composition of reduced fat sour cream reaches 30%.

However, the rationale for using both whey protein concentrate and hydrolyzed whey concentrate in reduced fat sour cream technology should be considered comprehensively. Whey protein concentrate ensures an increase in the biological value of the finished product and contributes to the stabilization of acidity during production and further storage. At the same time, the use of hydrolyzed whey concentrate, in addition to stabilizing acidity, makes it possible to obtain a product with a mass fraction of total solids and taste qualities corresponding to such the full-fat analogue as sour cream with fat 18–20%, but with an insignificant decrease in biological value.

Conclusions

1. The rational doses of milk protein concentrate in the composition of reduced fat sour cream, which ensure the achievement of the recommended value of titrated acidity of 60–75 °T in 6–8 hours of fermentation, for the selected protein ingredients are the following: skimmed milk powder, 1%; sodium caseinate, 0.5%; caseinate calcium, 0.75%; whey protein concentrate, 1%; hydrolyzed whey concentrate, 30%.
2. The use of milk protein concentrate allows to stabilize the acidity of the product during storage for 5 days. The most uniform distribution of moisture in the matrix of the protein

clot was observed for the sample with 1% whey protein concentrate, while the best adsorption of free moisture was noted for the sample with 30% hydrolyzed whey concentrate. The protein content is the largest in samples with caseinate calcium, CWP, and hydrolyzed whey concentrate and is 3.4, 3.38, and 3.22%, respectively, while the total solids is the largest in the sample with 30% of hydrolyzed whey concentrate. A comprehensive quality indicator was calculated, which is the highest for reduced sour cream samples with 1% whey protein concentrate and 30% hydrolyzed whey concentrate.

3. Addition of 1% whey protein concentrate to reduced fat sour cream increases biological value by 1.3%, while using 30% hydrolyzed whey concentrate decreases it by 3.5%. Thus, whey protein concentrate is a biological enricher with moderate technological properties, while hydrolyzed whey concentrate is a highly effective technological ingredient that allows to obtain an analogue of a full-fat sour cream, with an insignificant decrease in biological value.
4. The perspective of further research consists in scientific substantiation of recipes of reduced fat sour cream with taste-aromatic ingredients of plant origin.

Acknowledgments. The work was carried out at the National University of Food Technologies (Kyiv, Ukraine) within the framework of the state research projects "Implementation of resource-saving methods of modifying the functional and technological characteristics of milk whey in the technologies of food products for targeted purpose" (state registration number: 0120U100868) and "Scientific substantiation of resource-efficient technologies of food products enriched with multifunctional ingredients" (state registration number: 0120U102556).

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Nutritional and biological value of dried champignon powder

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Abstract

Keywords:

Champignons
Proteins
Amino acids
Semi-finished
products
Safety

Article history:

Received 20.06.2022
Received in revised
form 19.09.2022
Accepted 1.12.2022

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Introduction. The aim of this study is to evaluate the nutritional and biological value of dried champignon powder in the indices of quality and safety.

Materials and methods. The nutritional and biological value of dried champignon powders, obtained by the methods of low-temperature drying (45 °C) and subsequent disintegration, were studied in terms of the biological value of proteins and their factional distribution, ratios of essential and non-essential amino acids, their balance and digestibility.

Results and discussion. More than two thirds of all proteins in semi-finished products made from mushrooms are represented by factions with the high biological value: water-soluble albumens (45.6–46.8%) and salt-soluble globulins (23.1–26.7%). In frozen semi-finished products, this ratio would reach 80%, running over the content of the noticed factions in fresh mushrooms. So, the complexes of proteins and high polymers are partly ruined under the temperature of drying 45 °, with subsequent release of proteins and their dissociation, which led to the increase of the biological value of product. Conversely, after drying at this temperature, the share of insoluble proteins increases twofold in comparison to fresh mushrooms, which showed the inexpedience to use the high temperatures to process mushrooms.

The dried champignon powder contained all eight essential amino acids, which comprises about 46% of their total amino acids amount. Otherwise, the sum of non-essential amino acids scores 54%. These data are the important index of dried champignon powders due to the well-known fact that the maximal biological effect of food proteins is achieved at the ratio between essential and non-essential amino acids equal to 42:58, which is practically the same as the results of our research (46:54). According to the calculated amino acid scores, the amount of all amino acids exceeds the level of the reference protein recommended by the World Health Organization. Based on the coefficient of amino acid score difference, it was determined the nutritional and biological value of protein of dried champignon powders counting 51.8%, which is quite a high index.

The sensory characteristics of dried champignon powders appeared to be satisfactory. Microbiological evaluation showed the safety of the finished mushroom powder and its stability during the storage.

Conclusions. The knowledge about the protein components of dried champignons, their nutritional and biological values and the possibility to use them as powdered product was significantly expanded.

DOI:10.24263/2304-
974X-2022-11-3-9

Introduction

The human body does not practically contain the protein reserves. Meanwhile, all the vital processes are connected with its biological transformations on the level of cells and tissues, and with its ability to interact with unexceptionally all substances creating the complexes to constitute the base of a live organism (Nelson and Cox, 2017). One of the most essential sources of proteins are cultivated mushrooms that contain more than 35% of protein (in terms of dry matter), all the essential amino acids, unsaturated fatty acids, vitamins and trace elements (Asao et al., 2017). The modern food science considers them as the possible source of biologically active substances for food industry (Martinez-Medina et al., 2021; Stojković et al., 2014), in particular for creating the food additives capable of increasing the immunity to infections and oncologic diseases (Meera et al., 2009; Wasser et al., 2000), owing to the fact that anti-bodies formation is the modified process of normal biosynthesis of globulins (Haeney, 1994).

Production of cultivated mushrooms is considered one of the main tendencies in food industry to be constantly expanding (Bakratsas et al., 2021; Ferdousietal, 2020; Ivanov et al., 2021), primarily due to champignon and shiitake growing (Calvo et al., 2016; Martinez-Medinaetal., 2021; Shelke and Badhe, 2021; Stabnikova et al., 2010; Yurchak and Sharkova, 2023). Champignons contain about 3 percent of lipids, more than half of which are neutral fats. Their acid number is approximate to the similar index of plant oils, thanks to the high amount of free fatty acids that comprise more than 17% of the general lipid amount. These are butyric and acetic acids, along with oleic and stearic ones (Ribeiro et al., 2009). It is very important that mushrooms and their active compounds possess anticancer properties. Upon studying the influence of champignon chemical substances on the protein that damages the human DNA, there was revealed that the champignon components show far stronger effect than the standard pharmaceutical inhibitors (Shelke and Badhe, 2021). Along with that, cultivated mushrooms are low fat, low-calorie foods that, unlike the wild forest mushrooms, are free from heavy metals, radionuclides, and nitrates. They are considered to be the delicacies for cookery and used in many cuisines as the so-called ‘vegetable meat.’ The techniques and technologies of up-to-date level allow extracting antimicrobial, antioxidant, anti-allergenic substances and various nutrients in order to fortify the traditional food bases (Ramos et al., 2019). Important is the fact that the mushroom protein, in case of being processed by the certain technologies, would be well absorbed by the human body (Gonzálezetal, 2020).

Mushrooms have the short term of storage and microbiological and fermentative processes are continued in mushroom fruiting bodies after harvesting. All this makes it necessary to consume or process mushrooms immediately after they are harvested. To increase the shelf life of mushrooms, it is possible to use their drying, and convective drying followed with biomass grinding as the most wide-spread and effective technology for mushroom treating (Waldeetal, 2006). Therefore, the convective low-temperature drying method was chosen to obtain the powdered champignon product as the material for research.

An analysis of the literature data showed a limited number of research studying the amino acid composition of mushroom proteins, the ratio between essential and non-essential amino acids and comparison with the reference protein proposed by WHO (Dietary Protein, 2011). The objectives of the present research were to study protein component of dried at low temperature champignon powders to expand their usage in food technologies.

Materials and methods

Dried champignon powder

The dried champignon (*Agaricus bisporus*) was the subject of the research. The mushroom fruit bodies were washed, sliced, and dried by convective method at a temperature of 45 °C during 340 minutes. Dried champignons were then grounded to the particles with size of 100–150 microns and protein fractional distribution was determined in obtained powder. The calculations of amino acid scores to evaluate the level of protein utilization in human body were done.



Figure 1. Champignons and dried champignon powder

Determination of dry substances content

The content of dry substances was determined by differential refractometry using IRF-454 B2M refractometer (Laboratornatekhnika Ltd., Kharkiv) (Hernandez et al., 1998)

Determination of protein and amino acid content

The total amount of proteins, their qualitative and quantitative composition were determined using the capillary electrophoresis by the method of (Redweik et al., 2012).

Determination of total carbohydrates content

The content of total carbohydrates was determined by the methods of ion analysis using the chromatograph Bioscan 817 (Metrohm, 2023). To prepare the specimens for analysis, mushrooms were powdered to homogenous mass and placed into the automatic sampler of the chromatograph.

Determination of cellulose content

The amount of cellulose was determined by the gravimetric method: after oxidation, dissociation and dissolving various chemicals contained in mushrooms, cellulose residue was thenceforth removed, dried and weighed (Kumar and Turner, 2015).

Determination of factional composition of mushroom protein

Mushroom proteins were fractioned in different media: albumens in water; globulins in 1 M NaCl and 0.1 M phosphate buffer (pH 6.8); glutelins in 0.1 N NaOH; prolamins in 70 % ethyl alcohol. The samples of disintegrated products were introduced into the correspondent media, with the ratio between mushroom mass and the solvent 1 : 3 for determination of albumens and globulins; 1 : 2.5 for glutelins and prolamins; then the samples were centrifuged during 15 minutes at 6,000 rpm. The precipitate was then washed, and the volume of extract was added to 150 ml with washing water. The content of protein substances in extracts and the precipitates was determined by the method (Redweik et al., 2012).

Microbiological analysis

Microbiological analysis of bacterial contamination of dried champignon powders (particularly the presence of pathogenic microorganisms, bacteria, yeast and moulds) were carried out by quantitative accounting of contaminants on solid media (Tarabees et al., 2015).

Samples (25 g) of champignons were placed in 225 ml buffered peptone water and homogenized for 30 seconds in a lab blender. Decimal serial dilutions were prepared up to dilution 10^{-7} in sterile Ringer's solution and plated on selective agar media (Schill et al., 2021).

The quantities of mesophilic aerobic and facultative anaerobic microorganisms, bacteria of *Escherichia coli* group, pathogenic bacteria *Salmonella*, and moulds in dried mushroom powder were enumerated by methods (Schill et al., 2021).

Results and discussion

Characteristic of proteins of dried at low-temperature mushrooms

It is a well-known fact that proteins, regarding their solubility in different media, are categorized into four classes – albumens, globulins, prolamins and glutelins (Garidel, 2013). Albumens, or water-soluble proteins, are characterized with the highest nutritional and biological value. They are transformed in the human body with the minimal energy losses and therefore are the most balanced by their amino acid content. Globulins, or salt-soluble proteins, are also outstanding by their biological value, but they are mostly limited by the amount of sulfur-containing amino acids. The two other factions, alcohol- and alkali-soluble proteins (glutelins and prolamins, respectively) lack some essential amino acids, so they are harder exposed to proteolytic enzyme action and have lower nutritional value.

The scientific literature does not currently have any data about the protein fractional composition of dried champignon powders; therefore, it was one of the main tasks in the present work. Since the champignons, as well as the other types of plant raw materials, can be processed by different ways, comparative analysis of mushrooms after freezing, after thermal treatment, and after low-temperature drying were done (Table 1).

These results confirm the expedience of obtaining the dried champignon powders, owing to the fact that 70% of protein substances are albumens and globulins, i. e. proteins of high biological value (Martinez-Medina et al., 2021; Shelke and Badhe, 2021; Stojković et al., 2014). The data present in Table 1 show that the factional composition of champignon proteins significantly depends on the method to process the raw material. In other words, upon selecting the certain method of technological effect, it is quite possible to predict the increased ratio of the protein factions most valuable in terms of their biological activity, albumens first of all, and thenceforth reduce the part of the insoluble residue.

Table 1
Effect of the method to process champignons on their protein fractional composition

| Procession method | Mass part of protein faction, % of the total protein mass | | | | |
|---|---|--------------|----------------|-----------------|-------------------|
| | Water-soluble | Salt-soluble | Alkali-soluble | Alcohol-soluble | Insoluble residue |
| Fresh mushrooms | 43.6±1.6 | 24.0±0.5 | 12.8±1.1 | 5.2±2.4 | 14.4±0.5 |
| Mushrooms after freezing (-28 to-35°C) | 52.8±0.9 | 26.6±0.7 | 11.9±0.7 | 4.4±0.3 | 4.3±1.9 |
| Mushrooms after thermal treatment (85–90°C) | 33.5±2.2 | 20.4±1.4 | 8.8±0.9 | 6.3±0.8 | 31.0±1.4 |
| Mushrooms after low-temperature drying (45°C) | 46.4±0.4 | 24.9±1.8 | 10.4±0.15 | 3.08±1.2 | 15.0±1.6 |

In this case, the most efficient is freezing of mushrooms at temperatures of -28 to-35°C, using the quick freezing method, in which the share of albumens increased by 13.8%, and the share of the insoluble residue decreased by 28.7%. This can be explained by the fact that upon the temperature shock to which all mushroom cells and tissues are exposed while the temperature is falling to -35 °C, the firmly aggregated protein molecules composing the insoluble residue get freed and attain the ability to dissolve in water, consequently gaining the share of albumens and easily-soluble globulins.

Champignons dried at a low-temperature had approximately the same factional composition as after freezing; they contained the prevalent amount of easily soluble factions (79.4% in frozen mushroom and 71.3% in low-temperature dried ones). It would predictably increase the level of their digestibility and absorption by the human body.

On the contrary, champignons dried at high temperature were subjected to thermal destruction with the formation of insoluble protein-polysaccharide complexes, with a decrease in of water-soluble proteins by 27.8% and an increase of insoluble residue by 48.4%.

Amino acid content of proteins in dried champignon powder

The biological activity of food proteins is dependent on their amino acid content. The introduction of amino acids into nutrition is now becoming increasingly important (Asao and Asaduzzaman, 2017). Therefore, it is advisable to study the amino acid composition of low-temperature dried champignons and compare the ratio of an essential and non-essential amino acids. For more complete information, the proportion of amino acids in free and bound forms was determined. Amino acid content of proteins in dried champignon powder including amount of amino acids in free and bonded forms are presented in the Table 2.

The proteins of champignon dried at a low-temperature contain all essential amino acids with a total amount of 9.83 mg/100 g of the products. The amount of the total non-essential amino acids was 11.57 mg/100 g of the product and counts 54.06% of the total amino acid.

The dried champignon proteins contain free amino acids, which is 0.725 mg/100 g of the product for essential and 0.686 mg/100 g of the product for those non-essential amino acids. It can be predicted that after special methods for increasing the bioavailability of mushrooms, the proportion of free amino acids will increase significantly.

The result of calculating the balance of the amino acid composition, that is, the ratio of the amounts of non-essential and essential amino acids, was very important. For most proteins of natural origin, it is about 0.55-0.6% (Yastreba and Pasichny, 2010). In our studies, this indicator is 0.85%, which indicates the predominant part of the non-essential amino acids.

Table 2

Content of amino acids in proteins of powdered champignon dried at a low-temperature, mg/100 g of the product

| Amino acids | Content of amino acid | Content of amino acid | |
|---------------------------------|-----------------------|-----------------------|--------|
| | | Free | Bonded |
| Lysine | 1.25 | 0.10 | 1.15 |
| Phenylalanine | 1.75 | 0.03 | 1.72 |
| Leucine | 2.25 | 0.13 | 2.13 |
| Isoleucine | 0.74 | 0.16 | 0.58 |
| Valine | 1.27 | 0.18 | 1.1 |
| Methionine | 0.42 | 0.00 | 0.42 |
| Threonine | 1.90 | 0.13 | 1.77 |
| Tryptophan | 0.26 | - | 0.26 |
| Total essential amino acid | 9.83 | 0.73 | 9.11 |
| Total non-essential acid | 11.57 | 0.69 | 10.89 |
| Total amino acid | 21.40 | 1.41 | 19.99 |
| Balance by amino acid scores, % | 0.85 | 1.05 | 0.83 |

Furthermore, the proportion between essential and non-essential amino acids (which shares, in our research, count 45.93% and 54.06%, respectively) is worth of re-evaluation, since it is the well-known fact that it is just this correlation to play the crucial role in establishing the good conditions for catabolic processes in body tissues. The maximal biological effect of food proteins may be reached in case of 42% of essential amino acids (Nelson and Cox, 2017); the rest 58% should fall to non-essential amino acids. According to our results, the correlation between non-essential and essential amino acids in dried champignons is approximate to these optimal indices.

Finally, yet importantly, the share of free amino acids in fresh mushrooms counts 0.537 mg/100 g of the product, whereas in dried ones it grows up to 1.411 mg/100 g of the product. In other words, due to the low-temperature drying, some bonded amino acids transform into free ones, which would increase the biological value of both mushrooms themselves and the products with their additives. This is correspondent to the conclusions of Avdieva et al. (2021).

According to the scientifically proven conception of valuable nutrition, the biological value of a product is determined by not only the amount and the ratio of separate amino acids, but mainly their balance and accessibility for proteolytic enzymes effect (Vetter, 2019). Therefore, to make the complete characteristics of the protein constituent in dried champignon powders, we conducted the necessary calculations and compared the obtained results to the amino acid content of WHO reference protein.

The amino acid scores of essential amino acids in dried champignon powder are presented in Table 3.

Regarding the calculations, the amount of practically all essential amino acids exceeds the level proposed by WHO. In particular, it seems typical for the following amino acids: lysine (score 106), phenylalanine (score 146), methionine (score 125), which play the important role in the human body functioning, alike to the other essential amino acids (Asao and Asaduzzaman, 2017): lysine, liable for restoration of muscle tissues and rehabilitation after stresses; phenylalanine, constructing material for neuromediators synthesis; methionine, relevant for chronic fatigue syndrome treatment.

Table 3
Amino acid scores in dried champignon powder in comparison with WHO reference protein

| Amino acids | WHO reference amino acid, mg/100 g of protein | Amino acid amount, mg/100 g of the product | Score, % | CAASD, % |
|------------------------|---|--|----------|----------|
| Lysine | 55 | 1.245 | 106 | 20 |
| Phenylalanine+tyrosine | 60 | 1.88 | 146 | 60 |
| Leucine | 70 | 2.25 | 150 | 64 |
| Isoleucine | 40 | 0.735 | 86 | - |
| Valine | 50 | 1.27 | 119 | 33 |
| Methionine+cystine | 35 | 0.94 | 125 | 39 |
| Threonine | 40 | 1.2 | 171 | 85 |
| Tryptophan | 10 | 0.26 | 122 | 36 |
| Total amino acid | - | 21.4 | | |

Note: CAASD, coefficient of amino acid score difference.

During digestion, practically all essential amino acids contained by foodstuffs, including dried champignon powders, transform into important biochemical substances to fulfill the specific functions in human body (Joye, 2019). In this case, isoleucine is the amino acid to limit the biological value of proteins (score 86%).

The data presented in Table 3 also allowed defining the grade of dried champignon powders proteins utilization with a help of calculating the coefficient of amino acid score difference. Actually, this is counted by subtracting the score of the limiting amino acid (isoleucine) from the score of any essential amino acid.

The average arithmetical coefficient of amino acid score difference in a mushroom semi-finished product is equal to 48.2%; respectively, the biological value of low-temperature dried champignon proteins is 51.8%. These data are correlated to the similar results presented in the work (Yastreba and Pasichny, 2010), in which the biological value of oyster mushrooms semi-finished products was estimated in 44-45%.

Sensory and microbiological characteristics of dried champignon powder

Table 4 represents the sensory characteristics of powders made from champignons.

Table 4
Sensory quality parameters of dried champignon powder

| Parameters | Characteristics |
|-----------------|---|
| Appearance | Fine-disperse, 100–150 microns, powder with moisture content of 8–12%, homogenous, without lumps |
| Taste and smell | Typical for fresh champignons, without any strange taste and smack, palatable, delicious |
| Color | From light-cream in case the caps are separated from legs to different hues of brown |
| Texture | Dependent on the mushrooms' maturity grade and homogeneity; with the optimal quality characteristics, is loose, homogenous, without lumps |

It should be noted that at a drying temperature of 45 ° C, the process of binding of volatile components (alcohols and ketones: L-hexanol, 3-heptanol, 3-octanol, 3-octanone, L-octene) presumably occurs, which impart a specific mushroom aroma to dried champignons and products prepared with their use (Zhang et al., 2022).

An important task is to ensure the microbiological safety of dried champignon powder both immediately after their production and during storage. The microbiological analyses were performed directly after obtaining the dried champignon powder and every three months throughout a year. The results are presented in Table 5.

Table 5
Microbiological characteristics of dried champignon powder during storage

| Microorganisms | Hygienic norms | Time of storage, months | | | | |
|----------------------------------|------------------|-------------------------|------------------|------------------|------------------|------------------|
| | | 0 | 3 | 6 | 9 | 12 |
| MAFAnM, CFU/g | $5.0 \cdot 10^4$ | $2.2 \cdot 10^2$ | $2.2 \cdot 10^2$ | $4.6 \cdot 10^2$ | $8.3 \cdot 10^2$ | $5.8 \cdot 10^3$ |
| <i>Escherichia coli</i> in 0.1 g | N/A | N/D | N/D | N/D | N/D | N/D |
| Moulds, CFU/g | $5.0 \cdot 10^2$ | N/D | N/D | N/D | N/D | N/D |
| Yeast CFU/g | $2.0 \cdot 10^2$ | N/D | N/D | N/D | N/D | $1.0 \cdot 10^1$ |

Note: MAFAnM, mesophilic aerobic and facultative anaerobic microorganisms; CFU, Colony Forming Units; N/A, not allowed; N/D, not detected.

The results of microbiological analysis show that the pathogenic bacteria of *Salmonella* genus (in 25 g of the product) were not detected in dried champignon powder; the bacteria of *Escherichia coli* group were not found, as well as moulds. Yeast were detected only in the sample stored for 12 months, otherwise their amount is sufficiently less than the hygienic norm. Thus, the highlighted method to prepare the dried champignon powders, which includes their drying with a temperature of 45 °C for 340 min, provides the level of the product's general microbial contamination by MAFAnM within the limitations and alongside oppresses the activity of harmful microorganisms.

Conclusions

The deficiency of protein foods is dramatically progressing; the animal proteins, as well as those obtained by microbiological methods, cannot provide their necessary amounts in diets. Therefore, the role of natural plant-origin proteins, as well as knowledge on their chemical nature, is sharply increased, which would create the preconditions to development of scientifically intensified technologies to process the protein containing raw materials and widely include them into the food technology. In this viewpoint, typical for many countries are the increasing scales of growing and using the cultivated mushrooms, regarding the high amounts of their biologically active substances to express the various pharmacological impacts. Among the cultivated mushrooms, champignons (*Agaricus bisporus*) occupy the priority place.

The most important factors to define the selection of mushroom raw materials for obtaining the high-quality semi-finished products are the proteins, particularly their ratio, biological value, amino acid balance, compliance of essential amino acids with the WHO reference protein, and also sensory characteristics that satisfy both the requirements to main technological processes and the consumer's needs.

The results of theoretical and experimental researches presented in this work are believed to expand the knowledge about the protein components and the biological value of

champignons, to prove the expedience to process them into powdered products to fortify different food mediums in order to increase the protein ratio. These fortified foodstuffs would become an efficient remedy for both the correction of diets and prevention or additional treatment of alimentary-originated diseases. Henceforth, the studies of mushroom cultivation, improving the technologies of their procession and application as food supplements or healthy foodstuffs remain relevant for nowadays and for the years to come.

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Role of precision agriculture in food supply

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Abstract

Keywords:

Food security
Sustainable
Agrotechnology
Cyber threats
Precision
agriculture

Article history:

Received
23.08.2022
Received in revised
form 16.10.2022
Accepted 1.12.2022

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DOI:

10.24263/2304-
974X-2022-11-3-10

Introduction. The aim of our research is to provide an overview of the role and challenges of precision agriculture, to examine the current situation, in particular its impact on sustainable food production.

Materials and methods. The study is descriptive and used scientific secondary data as the primary source. The authors also conducted a primary research of farmers in Hungary in 2022 what they think about the role of precision farming. The primary research method is a questionnaire survey.

Results and discussion. Precision farming is a management approach that focuses on (near real-time) observation, measurement, and responses to variability in crops, fields and animals. Precision farming means the practical appearance of digitized agriculture, the use of digital solutions in agriculture, where developments are directed to how to manage in a more competitive way, to increase efficiency, while also placing great emphasis on environmental sustainability. Precision farming is increasingly used in agriculture today. The demand for agricultural products will grow dynamically over the next few decades, and this can be met by more efficient production.

On the Internet, when we type the term of precision agriculture we will get 147 million search results.

In our research, according to 81% of respondents, precision farming is very important. In recent years, the development of precision agricultural technology, mechanization and agricultural informatics has undergone significant development. More than half of the farmers use some kind of precision support system. Nearly 70 percent of respondents think that precision technology systems are too expensive. 31 percent of farmers would like to have more knowledge about precision technologies, mainly concerning productivity (yield, quality, etc.), plantation condition (plant growth status, soil analysis, etc.) and the distribution of inputs (irrigation water, organic fertilisers, fertilisers, etc.). More than half of the farmers think that policy makers in the industry (financial support, legal environment, etc.) should take action to make precision farming more accepted in practice and they think that it would also be important to deal with it more intensively in education. Farmers are open to precision solutions, but there are challenges to effective spreading.

Conclusions. The competitive future of agriculture is influenced by digitalisation and the use of precision agriculture. Precision agriculture is becoming increasingly popular in practice, as it can make a major contribution to sustainable food production.

Introduction

Agriculture is the production of material goods, a major branch of the economy that produces food and industrial raw materials.

The development of agriculture is characterised by three eras. According to Jóri (2017), the first, the pre-industrial era of agriculture, lasted from pre-Christian times until the 1920s. Self-sufficient, small-scale, labour-intensive farms required approximately one hectare of land to produce one person's food. The second phase, the period of industrial agriculture, lasted from 1920 to 2010. Tractors, combine harvesters, fertilizers and hybrid seeds allowed the emergence of large-scale commercial farms. The productivity of these developments meant that as little as half a hectare was enough to feed five people. The third phase is taking place today, when a large amount of data for production is available through satellite systems and sensors on machines and plants. The large amount of data and the “Internet of Things” allow to analyse many sources of information through various intelligent software, thus helping farmers. If we look at the impact of agricultural development on mechanisation, the first period (from the early 1900s) is characterised by the advent of tractors, increased efficiency, the need for manual labour and low productivity. The second period is the so-called green revolution (from the 1950s), when new agrotechnical practices, use of fertilisers, pesticides, seeds of high quality and increased production have emerged. From the third era, with the advance of mechanisation (from the 1990s), precision agriculture was introduced, i.e. automated steering systems (optimised mechanisation, minimum overlap), crop mapping (objective base data), variable rate application (input optimisation), telemetry (machine monitoring) and data processing. Then the use of smart electronic tools became more widespread and digitalisation has now reached the agricultural sector. It has proven economic effect due to the steep implementation of digital decisions and tools in managerial processes (Remeikiene et al., 2021; Roshchuk et al., 2022). Thus, in the fourth era (from 2010), digital agriculture can be seen in practice, involving the use of real-time farm management systems, value-added services, automation capabilities, advanced processing and food value chains (data platforms) (Kireyeva et al., 2021; Vasa-Trendov, 2020). These advanced digital solutions in the agriculture sphere can significantly mitigate the problem of food security (Vasylieva and James, 2021) and social security respectively via the essential impact of the consumer food expenditures on the level and quality of life, especially low-income groups of the population (Mishchuk et al., 2018).

But what does precision agriculture mean and what are the characteristics of precision farming?

Precision agriculture and precision farming are generally regarded as the same thing. However, the term precision agriculture, often abbreviates PA, is more widely used.

Although more complex definitions exist, the simple description of the precision agriculture is a way to “apply the right treatment in the right place at the right time” (Gebbers and Adamchuk, 2010). It is a farming management concept based upon observing, measuring and responding to inter and intra-field variability in crops or in aspects of animal rearing. The first actual definition of PA came from the US House of Representatives (European Parliament, 2014), which defined PA as “an integrated information- and production-based farming system that is designed to increase long term, site-specific and whole farm production efficiency, productivity and profitability while minimizing unintended impacts on wildlife and the environment”. Such a definition focused on “whole-farm” management strategies using information technology, highlighting the potential improvements on production while reducing environmental impacts. In addition, it already envisioned that PA

was applicable not only to cropping systems, but to the entire agricultural production system (i.e. animal industries, fisheries, forestry) (Gál et al., 2013).

According to ISPA (2019) precision agriculture (PA) is a management strategy that collects, processes and analyses temporal, spatial and individual data and combines it with other information to support farmer decisions based on estimated variability to improve the resource use, productivity, quality, profitability and sustainability. In a 2016 report on how big data will revolutionize the global food chain, McKinsey & Company define precision agriculture as: “a technology-enabled approach to farming management that observes, measures, and analyzes the needs of individual fields and crops”. According to McKinsey (Magnin, 2016), the development of precision agriculture is shaped by two trends: “big-data and advanced-analytics capabilities on the one hand, and robotics (aerial imagery, sensors, and sophisticated local weather forecasts) on the other”.

There are many other definitions of precision agriculture in the literature. According to Husti (2018), “A modern agricultural management concept using digital techniques to monitor and optimise agricultural production processes. The aim is to reduce costs and environmental pressures and to produce more and better food raw materials. It will be achieved through a specific combination of new sensor technologies, satellite navigation and positioning, and the Internet of Things (IoT).” Husti (2018) thinks that the aim of precision farming is to produce good quality and safe food by using available resources (feed, water, energy, etc.) as efficiently as possible. Of course, this is no different from the objectives of conventional farming, but the difference is that the efficiency of information gathering is improved by the use of digital technologies. Precision farming makes farming more regulated and precise. Simply, it differs from the traditional approach in that it allows decisions to be made per square metre or even per plant/animal. This in turn has a positive influence both on the ecological consequences of the agriculture companies’ activity and on their sustainable development (Piwowar, 2020; Przekota et al., 2020).

According to the European Parliament (2014), PA nowadays is seen as an “environment friendly system solution that optimizes product quality and quantity while minimizing cost, human intervention and the variation caused by unpredictable nature”. PA allows seamless data interchange between farmers, suppliers, service providers, authorities, processors, and resellers of agricultural produce. This makes it possible to trace back food production to virtually each square meter of a farmer’s field. The European Parliament’s (2016) report on precision agriculture and the future of farming in Europe defines precision agriculture as “a modern farming management concept using digital techniques to monitor and optimize agricultural production processes”. The key point here is optimization. Instead of applying an equal amount of fertilizers over an entire field, precision agriculture involves measuring the within-field soil variations and adapting the fertilizer strategy accordingly. This leads to optimized fertilizer usage, saving costs, and reducing environmental impact.

An accurate assessment of the situation of precision agriculture is difficult, but the surveys the definition and categorisation of the elements of precision farming, which makes it difficult to comparing the results because very few places collect data on it on a regular basis. The importance of the subject has led to an increasing number of questionnaire surveys and analyses based on data from input material and machinery distrib. According to 234 studies published between 1988 and 2005, the use of precision farming technologies was economically profitable in 68% of cases on average (Griffin and Lowenberg-DeBoer, 2005).

Gebbers and Adamchuk (2010) think that precision agriculture becomes a management practice of increasing interest because it links to key drivers directly related to worldwide issues such as sustainable agriculture and food security. Takácsné and Takács (2022) believes that if precision agriculture can spread faster worldwide, it can result in both individual and

social utility coincidences that promote sustainability in a wider meaning. According to Nassar et al. (2022), Non-Governmental Organizations (NGOs), whether international (INGOs) or local (NGOs), are the primary engines of humanitarian assistance in almost all national economies. Food security and these organizations are inextricably linked. The main objective of the study of Nagy and co-authors (2017) is to identify key determinants that influence agricultural productivity to assure food security, as well as to analyze domestic and foreign trade in agricultural products.

Precision farming is a management approach that focuses on (near real-time) observation, measurement, and responses to variability in crops, fields and animals. It can help increase crop yields and animal performance, reduce costs, including labour costs, and optimise process inputs. All of these can help increase profitability. Precision farming contributes to the development of agricultural production and to the production of healthy food raw materials, while respecting environmental and ecological standards. It is based on the use of power equipment with positioning (GPS, RTK), machine-to-machine linkage and geo-information, remote sensing, data collection, data integration and data analysis. The technical prerequisites for precision farming are high-precision navigation and automatic steering of machinery. The advantage of automatic steering is that, when coordinated with other systems, they enable the machine to steer automatically. This further reduces human error, allows greater control over the driving and reduces overlap. One of the most accurate ways of doing this is through RTK, which enhances GPS-based tracking to give cm accuracy in determining the position of the machine. RTK is able to determine the position so accurately by coordinating satellite systems with the ground correction signal (Németh, 2014).

There are many ways to determine very precisely some of the parameters of agricultural field. Today, there are numerous possibilities to map fields with high precision to obtain detailed and site-specific information. Drones, planes and satellites use remote sensing to identify the features of the area. It is possible to work with yield maps, GPS-assisted soil surveys, “talking fields” maps or NDVI maps produced by nitrogen sensors. Real data such as soil nutrient levels, soil type, pH, pest emergence, etc. can be extracted. This fine data allows farmers to monitor changes in soil and crop conditions and react to events with lightning speed, after thorough and properly instrumented soil sampling (Kay et al., 2013).

Precision farming in the strict sense is when you work with site-specific information and apply materials site-specifically. Precision farming cannot be imagined without thorough data collection and processing, so software is as much a prerequisite as a GPS signal. At the same time, new technical and IT solutions are being developed every day. The competition for supply means that it is increasingly challenging for users on the practical side to keep up with technical developments and to create the conditions for their application. In Hungary, GPS guidance systems combined with automatic steering are the most widespread. With this solution, the tractor travels straight between two points, covering only the smallest area necessary, which saves fuel. If the farmer wants to sow at variable rates or apply fertiliser site-specifically, he needs information that gives a professional basis for the amount of material to be applied. Thus, the pillars of precision farming are agrotechnology, IT background and technical solutions.

Materials and methods

Materials

The study is descriptive and used secondary data as the primary international source. Our primary research method is a questionnaire survey. In September 2022, we asked 110 farmers in Hungary what they thought about precision farming. The questionnaire contained 18 questions.

Abbreviations

GPS (Global Positioning System). A satellite-based positioning system developed and operated by the US Department of Defense that operates independently of weather and time of day and provides three-dimensional positioning. In everyday usage, it generally refers to satellite positioning. The most advanced satellite system, GPS is the foundation of precision farming. It is mainly used for automated steering and landmarking in agriculture. GPS allows the machine to follow the same track several times with high accuracy. This minimises human error and makes work on the ground accurate and predictable.

- IoT (Internet of Things): A system of networked devices with unique identifiers.
- NDVI (Normalized Difference Vegetation Index): A normalized difference vegetation index, calculated from remote sensing images, used to characterize the state of vegetation.
- RFID (Radio Frequency IDentification): Radio Frequency Identification. A technology used for automatic identification and data communication based on the communication of a radio frequency transceiver unit with an RFID tag placed on the objects or products being monitored. An RFID tag (also known as a tag) is a small object that can be attached to or embedded in the object or product to be identified.
- RTK (Real Time Kinematics): Real time kinematic positioning with an accuracy of +/- 2 cm using correction signals.

Results and discussion

Precision agriculture in the word

Precision agriculture is present all over the world, but at very different rates. The concept has taken off in the United States and is now making its way into other parts of the world, including Europe (Table 1).

Table 1

Precision agriculture on Google

| Expression | Match (pieces) | | |
|----------------------------------|----------------|---------------|---------------|
| | 19. 11. 2018. | 25. 06. 2019. | 01. 12. 2022. |
| Precision Agriculture | 79,500,000 | 94,700,000 | 147,000,000 |
| Precision Agriculture Technology | 16,800,000 | 26,300,000 | 55,000,000 |

Source: based on Jóri (2019) and supplemented by own research

According to Meister Media Worldwide (Sulecki, 2018), the US and Canada are the leaders, with Europe in second place and South America (Brazil and Argentina) in third in the use of the precision agriculture. China is prominent in research on drones and sensors, mainly due to the growing governmental interest in environmental protection. The Netherlands, Israel and Ireland are also at the forefront of technological developments.

According to Riports and Data (2020), the global precision agriculture market was valued at USD 6.33 billion in 2020 and is expected to reach USD 17.05 billion by the year 2028. It is gaining fabulous popularity among farmers due to the increasing need for ideal crop production with limited available resources.

According to a report by Grand View Research (2022), the global precision farming market size was valued at USD 6.96 billion in 2021 and is expected to expand at a compound annual growth rate of 12.8% from 2022 to 2030. The growth of precision agriculture is attributed to the burgeoning proliferation of the IoT along with the use of advanced analytics by farmers. Numerous government initiatives are being undertaken in developing countries such as India, Sri Lanka, and Nigeria to encourage the implementation of modern precision farming technologies, thereby maximizing productivity. China and Israel signed a trade agreement in September 2017 worth USD 300 million to facilitate the export of environment-friendly Israeli technology to China. Moreover, an effective administrative framework is also enabling farmers to gain adequate knowledge of the proper use and maintenance of precision farming equipment.

As one of the world's largest food producers, Brazil has significant potential in the digital agriculture market. According to Cherubin and co-authors (2022), the principles and tools of PA started to be adopted in the late 1990s in Brazil. It can be seen in their research that research in precision agriculture has evolved substantially over the last 25 years in Brazil. Precision technologies have been mainly adopted in the production of large area crops such as soy, maize and cotton (Ferro and Oliveira, 2019). Automatic steering, yield mapping and differentiated nutrient allocation are used on 33 percent of agricultural land, but in the largest cereal-growing district, the use rate of automatic steering exceeds 60 percent. Even here, the use of drones is not widespread (6 percent).

In a 2018 survey of Kansas Farm Management Association (KFMA) members, 84 percent of 621 respondents said they use at least one precision technology (Griffin and Yeager, 2018). Automatic steering is the most widely used (68 percent), nearly half of farmers (47.8 percent) use staging, grid-based soil sampling and yield mapping is nearly 40 percent, and differential fertilization is used by a quarter of respondents (24.6 percent). Differential seeding is the least widespread (16.4 percent). Among U.S. corn, soybean, wheat, and cotton growers over 1,000 acres (about 405 hectares), the use of precision technologies is even higher (Thompson et al., 2018). 837 respondents have very high rates of yield measurement (93 percent) and automatic steering (91 per cent), followed by differential nutrient amendment (73 per cent) and precision soil sampling (60 per cent).

Statistically, China feeds 22 percent of the world's population with merely 7 percent of the arable land. China apply precision agriculture technologies since 2012. The technique is particularly important in Xinjiang, where more than 80 percent of the country's cotton is produced. High cost, lack of perceived benefits, and skills and capability required to adopt precision agriculture represent barriers to adoption (Kendall et al., 2017).

A questionnaire survey of farmers in western Canada (Steele, 2017) was able to assess 261 responses, representing nearly 1 million acres (approximately 405,000 hectares). 98 percent of respondents use GPS navigation and 79 percent use automatic steering. The use of automatic phase control is also widespread (73 percent), used mainly for spraying and to a lesser extent for nutrient replenishment and sowing. 60 percent of respondents said that they have a GPS-equipped combine, but only 48 percent produce a yield map. Differentiated application technology is mainly

used for nutrient replenishment (48 percent) and seeding (24 percent). Remote sensing crop monitoring is also quite widespread, based on satellite imagery (28 percent) or drone imagery (19 percent). 48 percent of respondents use precision farming solutions overall farm, while 37 percent use it on only part of the farm. In Ontario, a survey of agricultural service providers was conducted (Mitchell et al., 2018). More than 96 percent of the service providers are engaged in precision agriculture-related activities, of which grid- or zone-based soil mapping, differential nutrient application, and nutrient application map production are prominent (81 percent and 74 percent, respectively). Differentiated seeding planning is carried out by 58 percent of respondents, while differentiated crop protection applications are even less common (32 percent). More than half of the providers offer yield mapping services and 41 percent also produce cost/benefit maps. Nowadays Canada is one of the five major countries, along with US, China, Germany, and Israel, in precision agriculture. In 2021, Canada's market was valued at USD 870 million, an annual growth of 11.5%. During 2017-21, the market grew at a compound annual growth rate of 11.8% (GlobalData, 2022).

Europe

A 2016 European Union study shows how and in what direction the use of precision farming can influence the direction of the European Union and its common agricultural policy (Table 2).

Precision solutions are advantageous if they can be extended over a large area, developed continuously and easily, applied in all units of the plant, independent of the sector, easy to operate for the machine user and applied in a sustainable and environmentally friendly way. The application of precision farming requires an appropriate economic scale. The cost/input ratio requires a certain minimum farm size. In Europe, smaller farms are still predominant, as 86% of farms are smaller than 20 hectares. In contrast, the spread of precision farming technologies (due to the turnover) is observed in farms larger than 100 ha, i.e. around 25% of farms in the European Union use this technology (Jóri, 2019).

There has been considerable research in farmers' adoption of precision agriculture technologies. According to a study by the Boston Consulting Group (Kurth et al., 2018), a quarter of European farmers use precision agriculture. However, available data suggest that there are significant differences between countries and that the technology used is often limited to vehicle navigation.

Denmark is one of the few countries where data on the uptake of precision agriculture is available from the Danish Statistical Office (DST, 2022). Precision technology agriculture cultivated 76 per cent of the Danish agricultural area in 2022 compared to 73 per cent in 2021. It is especially the large farms that have embraced the technology, as users had an average area of 179 hectares compared to 87 hectares among all farms in 2022. Farms with precision driving now cover 2/3 of the agricultural area. The spread of precision agriculture by area is increasing for all technologies. However, a majority of all farms, 63 per cent, still do not use precision farming. Among farmers who do not use precision technology, 48 percent cite excessive costs as a barrier.

Barnes and co-authors (2019) investigated the prevalence of machine guidance and differential N application in five European countries: Belgium, Germany, Greece, the Netherlands and the UK. 44 percent of the 971 respondents did not use these technologies, 34 percent used only vehicle navigation, while 22 percent also used differential N application. Belgium has the lowest take-up rate, while England (34 and 26 percent) and the Netherlands (48 and 24 percent) have the highest. In both cases, the use of technologies was significantly influenced by the age and education of the farmer, the size of the cultivated area, the income and if the farmer used some other precision technology (innovative attitude).

Table 2

How does precision agriculture influence policies?

| Policy issue | Description | Effect on policy objective* |
|---|---|------------------------------------|
| Competitiveness of EU farming | Farm holdings will apply PA technologies to produce 'more with less', increasing the competitiveness of farm holdings and agri-food chains. Large farms will benefit the most. | + |
| Farm holding size and number | Farm size will increase because of the required investments in PA technologies and know how. The number of farms will go down, which is the current trend already. | = |
| Jobs on farms in primary production | The number of jobs on farm holdings will decrease due to the implementation of PA technologies, especially on farms where still a lot of work is done by low skilled workforces. | - |
| Skilled workforces | PA requires more farmers skilled in (ICT) and a mature services industry. | + |
| Business development in agrifood chains | PA offers many opportunities for service industry (sensor industry, ICT, IoT, machine companies) and food companies (processors, logistics, retail) when the PA market grows. | ++ |
| Multi-functional agriculture | Farm holdings will focus more on farming when they invest in PA technologies and know how. | =/- |
| Demographic and rural development | PA may slow down or stop the trend of people leaving rural areas in the EU for better life in cities because it creates new business opportunities and work for highly skilled persons. | + |
| Food security | Sensor based monitoring systems and Decision Support Systems (DSS) will provide farmers and stakeholders with better information and early warning on the status of crops and animals and improve yield forecasts. | ++ |
| Food safety | Sensor based monitoring systems and DSS plus track and trace systems will provide farmers, processors and other stakeholders with better information and early warning on quality of food products. | ++ |
| Sustainable production | PA technologies allow the production of 'more with less'. The use of natural resources, agrochemicals, antibiotics and energy will be reduced to the benefit of both farmers and the environment, thus in turn society. | ++ |
| Climate change and action | See sustainable production and food security. Farmers and stakeholders can detect effects of climate change on agricultural production in an earlier stage and take action. | + |

*++ and + are positive, = is neutral or unknown, - and -- are negative effects

Source: EPRS, 2016

According to Paustian and Theuvsen (2017), in Germany 30% of farms have adopted precision farming technologies.

In France, the Observatoire des Usages de L'Agriculture Numérique (Observatory of Digital Agriculture, 2017) collects data on precision agriculture. According to the information on the website, in 2017, nearly 1 million hectares of agricultural land were remotely sensed, of which about 85 percent was satellite imagery and 15 percent was drone or aircraft imagery. Thanks in large part to France's Naïo Technologies, more than 100 robots are used for weed control in arable vegetable production and more than ten in vineyards. About 4% of French field crop farmers use computer controlled variable rate input application, mostly for fertilizer. About 20% of farmland in France has professionally developed soil maps. Almost 1 million ha of farmland in France was managed with remotely sensed data in 2017. Roughly, 85% of the remote sensing is by satellite and 15% using drones or aircraft.

Precision agriculture technology is readily available in the Ukraine. According to Hrynevych and co-authors (2022), professionals working in the agro-sector need to gain an understanding of how this concept works and regularly update their knowledge of innovative technologies.

The majority of farms in Serbia are between 2 and 5 hectares, and only 16 percent of arable land is owned by larger farms and cooperatives. A further problem is that the average age of farmers on family farms is 59 years, which makes the adoption of precision farming technologies slow (Tagarakis et al., 2018). At the same time, Serbia is the only non-EU country that has access to satellite imagery from the EU's Earth observation programme (Copernicus). The practical application and promotion of precision farming is carried out in collaboration with the Krivaja Agricultural Society. Krivaja started precision farming on more than 2,000 hectares three years ago and officially became the first digital farm in Serbia in 2018.

When evaluating the uptake of precision farming in Europe, it should be noted that the average farm size in the EU is 17 hectares, which is one tenth of the average farm size in the US (175 hectares) and 47 times smaller than in Australia (800 hectares) (Dryancour, 2017).

Hungary

In the beginning, precision farming meant only information-based management applied to crop production. Advances in spatial information technology and rapid analytical techniques have laid the foundations for site-specific farming. The emergence of precision or site-specific agriculture in its present sense began in the 1990s in the world's developed agricultural countries (United States, England, Germany), but in Hungary it started to spread later, through satellite positioning. In the 2000s, the tools that still form the basis of precision farming were developed, based on the widespread use of GPS, the possibility of a high degree of automation of agricultural machinery and the emergence of advanced geographic information systems (GIS) (Jóri, 2017).

Today, the most intensive practical implementation of precision agriculture in Hungary is on arable land. Digital technologies are much better known and more frequently used in crop production and horticulture than in animal husbandry and livestock breeding. According to Halas (2017), „There is a very intensive growth in the number of dairy cattle farms practicing precision farming, with many countries now using digital technologies on large-scale farms. The first IT-enabled pig farms were established in Australia, followed by Western Europe and North America. Alongside Australia, Europe is still leading the way in research to develop the technology.”

According to Hadászi (2018b), precision farming is (also) a widespread concept in Hungarian agriculture, however, each machinery manufacturer develops precision tools for their own brand, which are not compatible with each other. Thus, the data collected by the machines, which are highly valuable for precision technologies, are not compatible with each other. Hungarian farmers do not have a single brand of machinery, so this isolation poses a problem for the spread of precision solutions. Precision technologies will only really work well in Hungarian agriculture if these developments can be integrated into a system for compatibility. “Farmers use only 20 percent of the extremely valuable data from machines.” Hadászi (2018a). It can be seen that the toolbox for precision agriculture is a mixed picture. It is not an easy task for farmers to find the optimal solution for them, as each farm has its own unique possibilities and conditions and there is currently no universal solution.

In 2018, the Institute for Agricultural Economics Research conducted a questionnaire survey to assess the IT skills of Hungarian farmers and company managers who are professionally involved in agricultural production towards the use of digital tools and information systems on their farms. The non-representative, voluntary survey yielded 760 valuable responses. 84 percent of respondents, 640 people, indicated the field crop sector as their field of activity (including grassland and field vegetable production). The farms typically cover less than 200 hectares (88 percent) and the online survey has shifted the age of respondents towards the younger age group. The presence of digital technologies and tools on farms is very low. The highest proportion (35 percent) of arable farmers use satellite positioning. 20 percent of the responding arable crop farmers indicated that they use a line guide or automatic steering. Differentiated application (e.g. sowing, fertilisation) is used by 11% of respondents, with even lower use of remote monitoring systems, crop sensors in the crop and yield mapping. The study of the Research Institute of Agricultural Economics provides an overview of the trends observed in the digitalisation of agriculture, and the domestic situation of precision arable crop production in Hungary. During the survey, they investigated how different information sources are used by farmers to obtain knowledge about PA; sought farmers’ opinions on the barriers and drivers to the diffusion of these technologies; recorded their judgement on the contribution of PA to sustainability; and collected their experiences (if any) following the adoption of these technologies. Based on their questionnaire surveys, it is unfavourable that some farmers (1-5 per cent, depending on the technology examined) have tools suitable for PA but do not use them, and approximately 70 per cent of the non-adopters do not plan to use any of the examined tools and technologies. The planned digital investments are of low value (typically below HUF 500,000, which is enough to buy at most sensors or accessories), but it depends on the farm size. Respondents aged between 31 and 40 years have better digital competences and the greatest willingness to invest. In 2018, 54 of the 615 respondents claimed to be involved in PA to some extent (Gaál and Illés, 2020).

We also made a primary research of farmers in Hungary in 2022 what they think about the role of precision technology. The respondents farm are from all Hungarian counties. The 52.3% of respondents have a degree, only one farmer has a primary school education.

93 of the 110 respondents are exclusively involved in crop production. 75% of farms has between 1 and 10 employees. 33 farms are between 100 and 499 hectares and 15 farms are more than 1,000 hectares in size. 58 percent of farmers use precision support system. 81 percent of respondents consider that precision agriculture is important. Nearly 70 percent of respondents think that precision technology systems are too expensive. 31 percent of farmers said that they would like to have more knowledge about precision technologies, mainly concerning productivity (yield and quality, etc.), plantation condition (plant growth status, soil analysis) and the distribution of inputs (irrigation water, organic fertilisers, and

fertilisers). 52 percent of the farmers think that policy makers in the industry (financial support, legal environment) should take action to make precision farming more accepted in practice. More than half of the respondents think it would also be important task to deal with it more intensively in higher education.

Overall, precision farming is becoming increasingly popular in practice. With the possibilities offered by the system, work can be done more accurately and at the right time, saving pesticides, fertilisers, other inputs and fuel, making farming more profitable and protecting the environment. The weaknesses of precision farming are that it is unfortunately very expensive and time-consuming to set up a complete system and that it requires the right skills to use the tools. A further weakness is that once a precision system is purchased, the buyer does not receive the necessary training to put it into operation after the purchase. Another disadvantage is that not all machines, systems and applications are available in Hungarian. This can cause difficulties for everyday users in agriculture.

The system risk is that it could cause problems with incorrect data management. A potential risk is a satellite or internet connection failure, for example, when a workflow with automatic steering fails. Such problems are most likely to occur in border areas or in places where you have to work in the cover of tall trees or a mountainside.

The future

In the coming decades, technology will develop a lot further and many new tools will help farmers to farm. The more tools we use connected as part of a system, the more efficiently we can work the land. A digital networked system will result in higher yield averages and better quality crops, as well as less inputs to the land, less greenhouse gas emissions to the atmosphere and a more environmentally friendly farming system than today. This is also crucial because the amount of arable land is steadily decreasing due to urbanisation and the growth of industry, and we are building on land where production used to take place. Some estimates suggest that by the turn of the century the world's population could reach ten billion and agriculture will have to support it. The logical solution to the loss of land and population growth is to maximise production capacity, which can only be achieved by using a complete digital network. Soon, robots and unmanned heavy machinery will begin to proliferate and replace human resources in a given position to do the most precise work possible with the help of sensors and IT systems (Tamás, 2017).

Robotics technology and artificial intelligence, which have been applied in some countries in the world, will be the future direction of precision agriculture development, but they need to be adapted to fit local conditions in different areas. As precision farming grows, so do threats, including cyber threats, which are on the rise as hackers are able to exploit this technology.

According to Grispos and Doctor (2022) cyber attacks against agricultural targets are not some distant threat; they are already happening. In 2021, for example, a ransomware attack shut down one-fifth of US beef processing plants. Similarly, an Iowa grain storage cooperative was targeted by a group who claimed to have stolen data from the cooperative. While previous attacks have targeted larger corporations and cooperatives, individual farms may also be at risk. The incorporation of IT technologies into farm equipment, from GPS-guided tractors to artificial intelligence, potentially increases the ability of hackers to attack this equipment. Moreover, while farmers may not be ideal targets for ransomware attacks, farms can be tempting targets for hackers with other motives, such as terrorists. For example, an attacker could exploit vulnerabilities in fertiliser application technologies, which could result in a farmer unwittingly applying too much or too little nitrogen fertiliser to a particular

crop. The farmer could then either end up with a smaller crop than expected or with over-fertilised land, leading to waste and long-term environmental consequences. Worst-case scenario could be a malicious actor taking full control of large machinery, particularly if it is carrying dangerous chemicals, in a highly populated area or along a busy road.

Conclusions

Precision farming is generally an information and technology-based farming system that identifies, analyses and manages spatial and temporal variability in fields for optimal productivity, profitability, sustainability and safety while rationalising production costs. The growing environmental awareness of the population requires changes in agricultural management practices to sustainably preserve the quality of natural resources (water, air, soil) while maintaining farm profitability. The practical areas of precision farming are not only crop, livestock and viticulture, but can also be applied to other sectors, such as horticulture, forestry, fish farming, biotechnology, etc.

In our opinion, precision farming is needed in Hungary to increase the output of agriculture in a meaningful way. Today, as a result of progress, various digital tools and the software that facilitates their use are available to almost all users in Hungary.

Precision agriculture typically involves the use of state-of-the-art machinery, and therefore the use and maintenance of the associated machinery and equipment requires appropriate expertise. The introduction of precision practices is an investment-intensive process, which is why their uptake by small and medium-sized farms is currently limited. Precision farming is a practical expression of digital farming, but it also raises the issue of farmers' inability to use agricultural information technology properly. Like all new technologies, the introduction of precision farming requires new skills from farmers.

In fact, precision agriculture can offer solutions to mitigate the adverse effects of climate change, to feed a growing population (food quality and crop safety), to protect the environment and to promote sustainability. Precision technologies can make a major contribution to sustainable food production, as efficient production also means a reduction in the emissions and ecological footprint of livestock production. At the same time, however, we must not overlook the need to look at the economical and economic context, in addition to creating new technical and technological development solutions.

The development of integrated systems, linking existing systems, is a key element for the future of agriculture. In our experiences, much progress has been made in the development of precision farming over the last decade, and precision farming has become accessible and good practice, but its full potential has not yet been exploited. In our opinion, Hungary is not lagging behind the world in the application of precision technologies, but a change of attitude is needed for all actors to spread them. To sum up, precision farming is becoming more popular and farmers are opening up to the opportunities offered by digitalisation, but the countries must pay more attention to the new risks. These threats also pose a risk to the food supply.

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Анотації

Харчові технології

Вплив натуральних структуруючих інгредієнтів на структурно-механічні та фізико-хімічні властивості сумішей морозива

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Вступ. Метою дослідження є вивчення функціонально-технологічних властивостей натуральних інгредієнтів у складі низькокалорійного морозива як потенційних стабілізаторів структури і заміників жиру.

Матеріали і методи. Досліджено суміші морозива з β -глюканами з вівса і дріжджів, з ферментованим і неферментованим пектиновмісним пюре з буряка. В'язкість сумішей вимірювали на ультразвуковому віскозиметрі Uniran типу 505, в'язко-пружні властивості – на приладі *Kinexus lab+*, поверхневий натяг – на тензіометрі KSV Sigma 700, активність води – на приладі AWM-10.

Результати і обговорення. За результатами проведеного дослідження встановлено, що β -глюкан вівсяний виявляє більшу технологічну активність у складі сумішей морозива з низьким вмістом жиру (2%), порівняно з β -глюканом дріжджовим, у тому числі при сполученні з розчинним пектином овочевого пюре. Ферментоване пюре з буряка, яке містить не менше 1,0% розчинного пектину, чинить найбільший вплив на структурно-механічні характеристики сумішей низькожирного морозива у всіх його комбінаціях з іншими структуруючими інгредієнтами. Суміші морозива з вівсяним β -глюканом і овочевим пюре на нижчих частотах вимірювання в'язко-пружних властивостей виявляють пружність, але після перевищення певного значення частоти структура руйнується і суміші виявляють більшу в'язкість, ніж еластичність, що дає змогу більш інтенсивно насичувати суміші повітрям під час фризеравання. Виявлено кореляцію між в'язкістю, активністю води і поверхневим натягом сумішей низькожирного морозива, що пояснюється міжмолекулярною взаємодією між макромолекулами гідроколідів та активним зв'язуванням вільної води комплексом низькомолекулярних і високомолекулярних сполук. Альтернативною заміною стабілізаційної системи Vianoks C45 (моно- і дигліцериди жирних кислот + полісахариди) у кількості 0,5% у складі морозива з низьким вмістом жиру є комплекс натуральних інгредієнтів – β -глюкан вівса і ферментоване пюре буряка у кількостях 0,5 і 15%, відповідно.

Висновки. β -глюкан з вівса і ферментоване овочеве пюре виявляють синергізм між макромолекулами β -глюканів і пектину овочів з утворенням комплексних тримірних структур у складі сумішей морозива з низьким вмістом жиру, які значно покращують в'язко-пружні характеристики, поверхневий натяг та активність води отриманих сумішей морозива.

Ключові слова: морозиво, β -глюкан, пектин, в'язкість, активність води, поверхневий натяг.

Ресурсо- та енергозберігаючі способи сумісної переробки побічних продуктів і напівпродуктів у спиртовому виробництві

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Вступ. Метою статті було дослідження й обґрунтування ефективності енергозберігаючих способів сумісної переробки спиртовмісних фракцій у колоні циклічної дії, підвищення ступеня очистки спирту від легких домішок.

Матеріали і методи. Дослідження проводили в типовій розгінній колоні і колоні циклічної дії. Витрати рідини контролювали за допомогою витратомірів постійного перепаду тиску, концентрацію етилового спирту і легких домішок визначали ареометричним і хроматографічним методами, ступінь вилучення домішок і кратність їх концентрування – розрахунковим методом.

Результати і обговорення. Використання запропонованих авторами способів забезпечує сумісну переробку побічних продуктів і напівпродуктів спиртового виробництва (головної та сивушних фракцій) в розгінній колоні циклічної дії, оснащеної лускоподібними тарілками із змінним вільним перерізом, завдяки якій можна отримати високоякісний ректифікований спирт, збільшити його вихід на 3,8–4,0% з однієї тонни умовного крохмалю, або на 10,8 % порівняно з відомим способом, і зменшити питому витрату пари на 40 % (від 20 до 12 кг/дал безводного спирту, введеного на тарілку живлення). Подовження часу контакту пари і рідини на тарілках колони до 40 с дає змогу цілком видаляти естери, на 25% збільшити ступінь вилучення альдегідів, а вищих спиртів сивушного масла і метанолу – на 40%. Запропоновані технічні рішення й обрані технологічні режими надають можливість підвищити ефективність розділення спиртовмісної суміші в декантаторі, на 26% збільшити кратність концентрування альдегідів та естерів, вищих спиртів сивушного масла – на 40%, метанолу – на 37 %, зменшити втрати етилового спирту з концентратом домішок, кількість спиртовмісних відходів, металоємність технологічного обладнання і собівартість ректифікованого спирту.

Висновки. Запропоновані способи дають змогу максимально очищати етиловий спирт від головних і проміжних домішок у колоні циклічної дії, отримати високоякісний спирт, зменшити енерговитрати та втрати спирту з відходами.

Ключові слова: *спирт, ректифікація, тарілки, колона, домішки.*

Екологічний пакувальний матеріал для хлібобулочних і кондитерських виробів на основі нової модифікації пектину

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Вступ. Одним із природних полімерів, який доцільно використовувати у виробництві біодеградабельних плівок, є пектин, модифікаційний потенціал якого на сьогодні не вичерпано з метою зміни його властивостей.

Матеріали і методи. Пектин, полівініловий спирт (ПВС, Е 1203), гліцерин (Е 422), олеїнова кислота. Паропроникність плівки визначали за BS EN 12086:1997, фізико-механічні властивості (міцність, МПа; подовження, %) плівок – на

універсальній випробувальній машині TIRAtest-2151. ІЧ-спектроскопію проводили на пристрої фірми Nexus-475 Nicolet.

Результати і обговорення. Ефективність проведеної модифікації пектину підтверджена за допомогою ІЧ-спектроскопії та елементного аналізу. Так, утворення амиду пектину можна оцінити за смугою $\nu(\text{C-N})$ при 1333 см^{-1} . На відміну від продукту реакції з амоніаком, з карбамідом утворення сольових груп чітко не простежується. Зникнення смуги деформаційних ножичних коливань NH_2 -групи при 1592 см^{-1} , а також зсув смуги валентних коливань C=O та C-N карбаміду може свідчити про утворення ковалентного зв'язку між карбамідом і пектином. Дані елементного аналізу свідчать, що етерифікація пектину амоніаком, як і карбамідом, відбулася. Результати дослідження фізико-механічних і бар'єрних властивостей показують, що міцність плівки збільшується з 20,0 до 32,4 МПа за умови збільшення вмісту модифікованого пектину амоніаком у складі плівки з 0,5 до 4,5%. Показник подовження плівки зростає за умови збільшення модифікованого пектину в складі плівки, а паропроникність зменшується зі збільшенням вмісту модифікованого пектину у складі плівки з 6,1 мг/(м·год·кПа) до 4,3 мг/(м·год·кПа). Пектин, модифікований карбамідом, здійснює аналогічний вплив на властивості плівки, як і пектин, модифікований амоніаком. Проте утворена плівка більш міцна, що пояснюється утворенням водневих зв'язків між вільною аміногрупою карбаміду та OH -групами полігалактоуронової кислоти.

Висновки. За допомогою ІЧ-спектроскопії та елементного аналізу підтверджено проведено модифікацію пектину амоніаком і карбамідом.

Ключові слова: біодеградабельний, пектин, плівка, покриття, паропроникність.

Антиоксидантні властивості водно-спиртових настоїв чайно-трав'яних композицій на основі гостролиста парагвайського

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Вступ. Мета дослідження – визначити антиоксидантну здатність водно-спиртових настоїв чайно-трав'яних композицій на основі гостролиста парагвайського (*Ilex paraguariensis*) та оцінити їх перспективність для створення алкогольних напоїв.

Матеріали і методи. Рослинна сировина: *Ilex paraguariensis*; *Camellia sinensis* (ферментований чай; частково ферментований чай; неферментований чай); контрольний зразок – водно-спиртова суміш міцністю 40% об. Антиоксидантну здатність водно-спиртових настоїв чайно-трав'яних композицій визначали за методом редоксметрії та pH -метрії; сенсорні показники – з використанням методу бальної оцінки.

Результати і обговорення. Визначено величину антиоксидантної здатності водно-спиртових настоїв чайно-трав'яних композицій: активна кислотність (pH) – 5,51–6,20 од. рН; окисно-відновний потенціал (ОВП) (Eh_{act}) – 101,00–157,70 мВ; енергія відновлення настоїв (RE_{inf}) – 112,88–145,76 мВ, що добре узгоджується з теоретичним значенням ОВП (Eh_{min}) – 241,60–270,58 мВ; енергія відновлення/окислення рослинної сировини (RE_{plant}) – 28,34–61,22 мВ. Оскільки водно-спиртові настої чайно-трав'яних композицій на основі мате характеризуються

високою енергією відновлення (RE_{plant} 61,22 мВ) і такими показниками, як бальна оцінка (9,63 бала), колір (світло-коричневий), аромат (деревний), смак (кисло-гіркий, з тривалим гіркуватим присмаком), то вони можуть бути рекомендовані в технології алкогольних напоїв у невеликих кількостях для закладів ресторанного господарства при виготовленні алкогольних напоїв.

У процесі купажування чайно-трав'яних композицій спостерігається підвищення показників сенсорної оцінки сумішей на основі *Plex paraguariensis*: чай ферментований/мате ($\omega, \%$ 75/25) – 9,67 бала; частково ферментований чай/мате ($\omega, \%$ 75/25) – 9,68 бала; неферментований чай/мате ($\omega, \%$ 75/25) – 9,71 бала. Розроблено рецептурний склад алкогольних напоїв раціонального складу: водно-спиртовий настій чайно-трав'яної композиції (ферментований чай/мате, або частково ферментований чай/мате, або неферментований чай/мате $\omega, \%$ 75/25) – 38,49%, бренді – 7,54%, ванілін 1:10 – 0,01%, цукровий сироп (65,8%) – 53,08%, кислота лимонна – 0,28%, «цукровий колер Е 150» – 0,6%, спирт етиловий і вода підготовлена – у розрахунку на міцність 20%.

Висновки. Для технології ресторанного господарства запропоновано застосування водно-спиртових настоїв чайно-трав'яних композиції на основі *Plex paraguariensis*, які володіють підвищеними антиоксидантними характеристиками та сенсорними показниками, для виробництва алкогольних напоїв.

Ключові слова: *гостролист парагвайський, Plex paraguariensis, чайно-трав'яна композиція, водно-спиртовий настій, алкогольний напій, антиоксидант.*

Застосування концентратів молочного білка при приготуванні сметани зниженої жирності

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Вступ. Обґрунтовано доцільність застосування білоквмісних інгредієнтів молочного походження в рецептурному складі сметани з вмістом жиру 10%.

Матеріали і методи. Кінетику сквашування кислотовершкових сумішей визначали за характером зміни титрованої кислотності. Мікроструктуру дослідних зразків сметани досліджували за допомогою світлового мікроскопа. Реологічні характеристики зразків низькожирної сметани вивчали із застосуванням ротаційної віскозиметрії.

Результати і обговорення. Раціональні дози молочно-білкових інгредієнтів у складі низькожирної сметани, що запобігають перекисанню вершків, структурують і стабілізують цей продукт впродовж п'яти діб зберігання, такі: сухе знежирене молоко – 1%, казеїнат натрію – 0,5%, казеїнат кальцію – 0,75%, концентрат сироваткових білків – 1%, концентрат гідролізованої сироватки – 30%. За ступенем гальмування процесу молочнокислого бродіння молочно-білкові концентрати у вказаних кількостях можна розташувати в такій послідовності: сухе знежирене молоко → концентрат сироваткових білків → казеїнат кальцію → концентрат гідролізованої сироватки → казеїнат натрію.

За результатами мікроструктурного аналізу зразків низькожирної сметани визначено, що одинвідсотковий концентрат сироваткових білків забезпечує належне утримання вологи в кисломолочному згустку та сприяє формуванню ніжної структури з дрібнодисперсними комірками, а використання 30-відсоткового концентрату

гідролізованої сироватки формує більш в'язку консистенцію продукту за наявності в ньому моноцукрів, які мають вищу адсорбувальну здатність вільної вологи. Доведено найбільшу структуруючу здатність казеїнатів і найсуттєвіший вплив сироваткових білків на тиксотропні властивості сметанного продукту. Проведено органолептичну оцінку та розраховано комплексний показник якості зразків низькожирної сметани та визначено зразки з одновідсотковим концентратом сироваткових білків та тридцятивідсотковим концентратом гідролізованої сироватки як такі, що мають найбільш привабливі органолептичні показники.

Досліджено хімічний склад зразків низькожирної сметани із сироватковими білками. Встановлено, що одновідсотковий концентрат сироваткових білків підвищує біологічну цінність на 1,3%, тоді як тридцятивідсотковий концентрат гідролізованої сироватки знижує на 3,5%. За результатами досліджень, концентрат сироваткових білків було віднесено до біологічного збагачувача з помірними технологічними властивостями, а концентрат гідролізованої сироватки – до ефективно технологічної добавки, що імітує показники якості аналогу із середньою жирністю 20%.

Висновки. Доведено технологічні переваги застосування сироваткових концентратів у складі низькожирної сметани як поліфункціональних інгредієнтів.

Ключові слова: сметана, жир, білок, сироватка, казеїнат, мікроструктура.

Хімічний склад журавлини болотяної (*Vaccinium oxycoccos*) для потенційного використання як функціонального інгредієнта

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Вступ. Мета дослідження полягала в тому, щоб визначити хімічний склад журавлини болотяної (*Vaccinium oxycoccos*) залежно від ґрунту вирощування.

Матеріали і методи. Аналіз проводився на стиглих плодах, зібраних у Румунії (повіт Сучава, комуна Кошна) на торф'яній ділянці. Мінеральний вміст визначали за допомогою сполученого мас-спектрометра (ICP – MS). Для визначення антиоксидантної активності використовували метод DPPH, вмісту поліфенолів – метод Folin Ciocalteu та аналіз HPLC.

Результати і обговорення. Вміст вологи в ягодах журавлини склав 84,1%, що відповідає даним інших досліджень. Отримано відносно низьке значення зольності – 1,38%, що відповідає низькому вмісту мінеральних речовин у ґрунті. Проте вміст мінеральних речовин у проаналізованих ягодах вищий порівняно з даними інших досліджень. Для більшості елементів спостерігалася позитивна кореляція між вмістом мінералів у ягодах і ґрунті. У досліджуваній журавлині зафіксовано значний вміст кальцію, близький до середнього значення, про який повідомлялося в інших дослідженнях. Вміст магнію та міді знаходився у межах, визначених іншими дослідженнями, а марганцю, заліза і цинку був нижчим. Вміст миш'яку, ртуті та стибію був нижчим за максимально затверджені ліміти, а свинцю – нижчим за ліміт виявлення.

Що стосується антиоксидантної здатності, відсоток інгібування вільних радикалів і загальний вміст поліфенолів у водному екстракті вищі, ніж в етанольному, середній вміст у досліджуваних ягодах, порівняно з іншими зареєстрованими даними, склав 340,78 мг/100 г у водному екстракті та 254,20 мг/100 г в етанольному. За даними

інших досліджень, у дикорослих плодах болотяної журавлини загальна кількість поліфенолів значно вища порівняно з культурними сортами.

Із поліфенолів варто відзначити високий вміст кверцетину – 0,39 мг/100 г і мірицетину – 0,23 мг/100 г. В етанолових екстрактах з'являється хлорогенова кислота – 0,42 мг/100 г, і п-гідроксибензойна кислота – 0,41 мг/100 г, що близько до даних інших дослідженнях. Проте спостерігалася присутність розмаринової кислоти – 0,12 мг/100 г, про що раніше не повідомлялося. У бензольному екстракті з'являється р-кумарова кислота – 0,27 мг/100 г. У журавлині торф'яній дрібній зафіксовано 5,98 мг/100 г вітаміну С, що підтверджує її антиоксидантну активність.

Висновки. За хімічним складом журавлина болотяна, зібрана у повіті Сучава, Румунія, подібна до журавлини з інших географічних регіонів, тому може розглядатися як ягода з високою антиоксидантною активністю.

Ключові слова: журавлина, *Vaccinium oxycoccos*, антиоксидант, поліфенол, аскорбінова кислота, кверцетин.

Харчова та біологічна цінність порошоків сушених печериць

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Вступ. Мета дослідження – оцінити харчову та біологічну цінність порошоків сушених печериць за показниками якості та безпеки.

Матеріали і методи. Досліджено харчову та біологічну цінність порошоків сух сушених печериць, отриманих методом низькотемпературного сушіння (45 °С) з подальшим подрібненням, за показниками біологічної цінності білків, їх фракційним розподілом, масовими частками незамінних і замінних амінокислот, збалансованістю та засвоюваністю.

Результати та обговорення. Різні фракції білків мають різну здатність до розчинності в організмі людини, що є одним із показників їхньої біологічної цінності. У порошках сушених печериць понад 2/3 усіх білків складають фракції, що мають найвищу біологічну цінність: водорозчинні альбуміни (45,6–46,8%), солерозчинні глобуліни (23,1–26,7%). У заморожених напівфабрикатах ця частка досягає 80%, перевищуючи вміст зазначених фракцій у свіжих грибах. Тобто, під впливом низьких температур комплекси білків з високополімерами частково руйнуються, вивільняючи білки і сприяючи їх розчиненню, що загалом підвищує біологічну цінність. Після термічного оброблення частка нерозчинних білків зростає вдвічі порівняно зі свіжими грибами та іншими напівфабрикатами, що свідчить про недоцільність використання високих температур при переробленні грибів.

У порошоків сушених печериць виявлено усі незамінні 8 амінокислот, що склало майже 46% їх загальної кількості. Сума замінних амінокислот становить 54%. Ці дані є важливим показником харчової та біологічної цінності порошоків, оскільки відомо, що максимальний біологічний ефект білків їжі досягається при співвідношенні незамінних і замінних амінокислот як 42:58, що близько до отриманих нами результатів (46:54). Відповідно до розрахованих амінокислотних скорів, вміст усіх амінокислот перевищує рівень еталонного білку, рекомендований FAO/WHO. За розрахунками коефіцієнта різниці амінокислотного скору КРАС визначено харчову та

біологічну цінність білку порошоків сушених печериць – 51,8%, що є досить високим показником.

Задовільними виявились органолептичні показники порошоків. За результатами мікробіологічної оцінки, патогенних мікроорганізмів (бактерій групи кишкової палички), пліснявих грибів не виявлено.

Висновки. Розширено спектр знань про білкову складову печериць, їхню харчову та біологічну цінність, доцільність використання в якості порошкоподібних напівфабрикатів низькотемпературного сушіння.

Ключові слова: *печериці, білки, амінокислоти, напівфабрикати, безпека.*

Економіка і управління

Роль точного землеробства в продовольчому забезпеченні

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2 – Будапештська школа бізнесу, Будапешт, Угорщина

Вступ. Метою дослідження є оцінка ролі та викликів точного землеробства, вивчення його поточного стану та впливу на стале виробництво харчових продуктів.

Матеріали і методи. Дослідження є описовим і використовує наукові вторинні дані як першоджерело. Автори також провели первинне дослідження думки угорських фермерів у 2022 р. про роль точного землеробства. Основним методом дослідження є анкетне опитування.

Результати і обговорення. Точне землеробство – це підхід до управління, який зосереджується на спостереженні (майже в реальному часі), вимірюванні та реагуванні на мінливість довкілля. Точне землеробство характеризує практичне виникнення цифрового сільського господарства, використання цифрових рішень, де розробки спрямовані на конкурентні способи управління, підвищення ефективності, при цьому значна увага приділяється екологічній стійкості. Попит на сільськогосподарську продукцію динамічно зростатиме протягом наступних кількох десятиліть, і його можна задовольнити більш ефективним виробництвом. За результатами пошукових запитів «Точне землеробство» («Precision farming») у мережі Internet отримується 147 млн результатів пошуку.

На думку 81% респондентів, точне землеробство є дуже важливим. За останні роки значного розвитку набули точна агротехніка, механізація та сільськогосподарська інформатика. Більше половини фермерів використовують будь-яку систему точної підтримки. Майже 70% респондентів вказують на занадто високу вартість прецизійних технологічних систем. 31% фермерів бажає мати більше знань про точні технології, зокрема про продуктивність (врожайність, якість тощо), стан насаджень (стан росту рослин, аналіз ґрунту тощо) та розподіл ресурсів (вода для поливу, органічні добрива тощо). Понад половина фермерів вважає, що адміністративний апарат галузі має вжити заходів щодо фінансової підтримки, правового середовища тощо для того, щоб зробити точне землеробство більш прийнятним на практиці, також важливо займатися цим більш інтенсивно у сфері освіти. Фермери відкриті для точних рішень, але існують проблеми для їх ефективного поширення.

Висновки. На конкурентоспроможне майбутнє сільського господарства впливають цифровізація і впровадження точного землеробства на практиці, оскільки воно може зробити значний внесок у стале виробництво харчових продуктів.

Ключові слова: *продовольча безпека, сталий розвиток, сільське господарство, агротехнологія, кіберзагроза, точне землеробство.*

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A manuscript should describe the research work that has not been published before and is not under consideration for publication anywhere else. Submission of the manuscript implies that its publication has been approved by all co-authors as well as by the responsible authorities at the institute where the work has been carried out.

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Introduction provides a rationale for the study (2–3 lines).

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Вимоги до оформлення статей

Мова статей – англійська.

Мінімальний обсяг статті – **10 сторінок** формату А4 (без врахування анотацій і списку літератури).

Для всіх елементів статті шрифт – **Times New Roman**, кегль – **14**, інтервал – 1.

Всі поля сторінки – по 2 см.

Структура статті:

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3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озеряно).
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 - Висновки (2–3 рядки).
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Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

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|--------------------------|----------------------------|
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2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

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(2013), *Svitovi naukovometrychni bazy*, Available at:

http://www.nas.gov.ua/publications/q_a/Pages/scopus.aspx

Cheung T. (2011), *World's 50 most delicious drinks*, Available at:

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Наукове видання

Ukrainian Food Journal

**Volume 11, Issue 3
2022**

**Том 11, № 3
2022**

Підп. до друку 1.12.2022 р. Формат 70x100/16.
Обл.-вид. арк. 12.31. Ум. друк. арк. 12.03.
Гарнітура Times New Roman. Друк офсетний.
Наклад 100 прим. Вид. № 24н/22.

НУХТ. 01601 Київ–33, вул. Володимирська, 68

Свідоцтво про державну реєстрацію
друкованого засобу масової інформації
КВ 18964–7754Р
видане 26 березня 2012 року.