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Contents

Characterization of aromatic compounds and antimicrobial properties of four spice essential oils from family *Lamiaceae*

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Abstract

Introduction. Representatives of the Lamiaceae family are widely used in the food industry as they are characterized by a high content of aromatic compounds.

Materials and methods. It was evaluated the chemical composition and antibacterial activity of essential oils of garden thyme (*Thymus vulgaris* L.), rosemary (*Rosmarinus officinalis* L.), spearmint (*Mentha spicata* L.), and sweet basil (*Ocimum basilicum* L.).

Results and discussion. The percentage ratio of volatile components obtained by GC-MS analysis of essential oil from garden thyme contains: thymol (37.90%) and γ-terpinene (19.44%). It has been determined eucalyptol (19.89%) and camphor (16.86%) in the essential oil of rosemary and carvone (50.23%) and limonene (13.90%) in spearmint oil, respectively. The differences in the quantitative and qualitative composition of essential oils and their aromatic components in relation to the previous researches may be probably due to different environmental and genetic factors, different chemotypes and the nutritional status of the plants as well as other factors that can influence the oil composition. *Escherichia coli* was the most susceptible bacterium strain. The essential oils of spearmint and rosemary possessed the most pronounced antibacterial activities against *Escherichia coli* (with inhibition zone: 32.00 mm and 30.00 mm).

Conclusions. The results obtained provide a basis for a thorough examination of the chemical composition and antimicrobial properties of various representatives of Lamiaceae family with a view to a wide usage in food technology.

Introduction

The family of Lamiaceae (also known as Labiatae) has very large distribution, containing about 236 genera and 6900 to 7200 species. Representatives of the Lamiaceae family are widely used for various purposes, but their most extensive usage is in the food industry as they are characterized by a high content of aromatic compounds. Sweeet basil, spearmint, rosemary, sage, oregano and garden thyme are only some of the species with wide usage in culinary production all over the world [22].

Garden thyme (*Thymus vulgaris* L.) is an evergreen herb, native to the southern Europe and the Mediterranean [20]. The plant has been used since ancient times as a culinary ingredient, to add flavor to cheeses [4, 2] and liqueurs [29, 26] and to flavor meats such as rabbit, boar, and lamb [12].

The herb garden thyme is pungent in taste and contains protein, crude fiber, minerals, vitamins, etc. [3]. The essential oil of garden thyme and the compound thymol have antimicrobial activity in vitro against *Escherichia coli* strains [7, 13]. Garden thyme essential oil is one of the most commonly used aromatic products in the home kitchens as well as in the food industry as preservatives and antioxidants.

A study including 21 essential oils and five pathogenic bacteria, demonstrated that the garden thyme had one of the most potent bacteriostatic and bactericidal effects against *Escherichia coli*, *Salmonella enteritidis*, *Listeria monocytogenes*, and *Staphylococcus aureus* [36].

Rosemary (*Rosmarinus officinalis* L.) is one of the most economically important plants of the family Lamiaceae. The name "rosemary" derives from the Latin words "ros", meaning "dew" and "marinus," meaning "sea" – "dew of the sea". Rosemary has been used in the culinary since decades. Native to the Mediterranean region, the plant is now widely distributed all over the world mainly due to its culinary, medicinal, and commercial uses including in the fragrance and food industries [21]. Both fresh and dried leaves of rosemary have been used for their characteristic aroma in cooking or consumed in small amounts as herbal tea, while rosemary extracts are routinely employed as natural antioxidant to improve the shelf life of perishable foods. The culinary, medicinal, and fragrance uses of rosemary are attributed to the vast arrays of chemical constituents collectively known as plant secondary metabolites [40]. Moreover, one group aromatic compounds are with small molecular weight, called essential oils which play vital role in the fragrance and culinary properties of the plant [15]. The application of rosemary in the culinary practice is related to the corresponding chemotype of the spice, which has pronounced flavoring properties.

According to Fu et al. [18] minimum inhibitory concentrations of rosemary essential oil ranged from 0.125% to 1.000% (v/v) and possessed significant antimicrobial effects against Gram-positive bacteria, three Gram-negative bacteria.

Spearmint (*Mentha spicata* L.) is an aromatic plant that can be used fresh or as dried leaves or powder, as a seasoning and flavoring herb, or traditionally as herbal tea [25]. In addition, spearmint essential oil has economic relevance due to its use in perfumery, confectionary, cosmetics and pharmaceutical preparations. The fresh and dried spearmint leaves have been used as a flavoring agent in various food products, including cheese and dough (Iranian yoghurt drink), chocolate, beverages, jellies, syrups, candies, ice creams, and chewing gum [32].

Spearmint essential oil had strong activity against *S. aureus*, *E. coli*, *Candida albicans* and *C. tropicalis* [35]. Besides its flavoring properties, spearmint is also widely used as an antimicrobial agent and as a preservative in food, mainly because of its oxygenated compounds [27, 11].

Sweet basil (*Ocimum basilicum* L.), is a culinary herb of major importance. Most culinary and ornamental basils are cultivars of the species *O. basilicum*, but other species are also grown and there are many hybrids between species [38]. Sweet basil can be dried or used fresh, similar to many other pot-herbs. It is best used fresh, as dried it will lose its flavor. Sweet basil leaves containing essential oil of distinctive aroma can be used both fresh and dried to spice up various kinds of meals. Apart of culinary use, sweet basil has been traditionally applied as a medicinal herb [33]. The presence of essential oil and its composition determine the specific aroma of plants and the flavor of the condiment [33]. Although essential oils in different basil cultivars are variable, prevalent components are monotherpenes and phenylpropanoids [28]. Fresh sweet basil leaves is used as an ingredient in various dishes and food preparations, especially in the Mediterranean cuisine. Due to its antimicrobial [9, 37] and insecticidal [8] activities and very pleasant aroma, sweet basil essential oil is widely used in the food.

Its usage in culinary practice is based on the possibility of fresh and dried leaves to emphasize meat and vegetable flavors, giving them a pronounced aromatic flavor. Most often aromatic components in fresh spices are obtained by low temperature extraction with vegetable oils used in culinary practice. The resulting aromatic oil substances are successfully used, such as salad dressings, spices for meat and vegetable soups, poultry and game dishes.

Due to the wide use of the Lamiacea spices in the food technology and the scarce information in Bulgaria about their aromatic composition and antimicrobial properties against foodborne pathogens, it have been involved the need for their further examination.

The aim of the present study is to characterize the aromatic components in the essential oils of four spices of the family Lamiaceae and antimicrobial properties against pathogenic bacteria, causing foodborne illnesses, with potential possibilities for their application in food technology.

Materials and methods

Plant Material

Garden thyme (*Thymus vulgaris* L.), rosemary (*Rosmarinus officinalis* L.), spearmint (*Mentha spicata* L.), sweet basil (*Ocimum basilicum* L.) were purchased from the merchant local market in Plovdiv. Samples were identified by an expert in Agricultural University of Plovdiv, Bulgaria.

The moisture content of raw materials was determined by drying to constant weight at 105°C [34].

Essential oils

The essential oils were obtained with modification of hydrodistillation for 150 min in the laboratory glass apparatus according to the British Pharmacopoeia [6].

The oils were dried over anhydrous sulfate and stored in tightly closed dark vials at 4 °C until analysis.

The GC-MS analysis was carried out with an Agilent 5975C MSD system coupled to an Agilent 7890A gas chromatograph (Agilent Technologies Inc., Santa Clara, CA). Agilent J&W HP-5MS column (0.25 μm, 30 m x 0.25 mm) was used with helium as a carrier gas (1.0 mL min^{-1}). The operational conditions were: oven temperature 35 °C/3 min, 5 °C/min to 250 °C for 3 min, total run time 49 min; injector temperature 260 °C; ionization voltage 70 eV; ion source temperature 230 °C; transfer line temperature 280 °C; solvent delay 4.25 min

and mass range 50 – 550 Da. The MS was operated in scan mode. One μL of the sample was injected into the GC/MS system at split ratio 30:1. The GC analysis was carried out using an Agilent 7890A GC system; FID temperature 270 °C. In order to obtain the same elution order with GC/MS, simultaneous triplicate injections were done by using the same column and the same operational conditions.

The identification of compounds was made by comparing their mass spectra with those from mass spectra libraries [1] and by comparing the literature and estimated Kovat's (retention) indices that were determined using mixtures of homologous series of normal alkanes from C_8 to C_{40} in hexane, under the conditions described above. The percentage ratio of volatile components was computed using the normalization method of the GC/FID peak areas.

Determination of antibacterial activity

As test microorganisms were used strains of pathogenic bacteria, reported as causing foodborne infections, intoxications and toxicoinfections. Antibacterial activity of essential oils was tested against Gram-positive bacteria – *Listeria monocytogenes* NCTC 11994 and *Staphylococcus aureus* ATCC 25093, and Gram-negative bacteria – *Escherichia coli* ATCC 8739 and *Salmonella enterica* subsp. *enterica* serovar Abony NCTC 6017. The selective growth media were: *Listeria* Oxford Agar Base /Merck/; Baird Parker Agar Base with Egg Yolk Tellurite emulsion supplement /Merck/, Rapid' *E.coli* 2 Agar /BioRad/ and Mac CONKEY Agar /Merck/, respectively.

The media were inoculated with 24-hour suspension of the bacterial species.

Melted and cooled to 45 °C selective media were inoculated with the tested microorganisms and next equally dispensed into Petry dishes. After setting of the media, sterile rings (Ø 6 mm) were placed on, and the amount of each sample (0.05 mL) was put into the rings. Petry dishes were incubated at 37 °C for 24 or 48h according to the bacterial spices, and then the distinct zone of growth inhibition (mm) around the rings was measured. The used inoculums have resulted as an actual concentration cells of *L. monocytogenes, S. aureus*, *E. coli*, *S. enterica* into the responding selective medium about 3×10^5 CFU/mL. The total plate count was estimated by the conventional plate-counting technique using appropriate dilution.

Results and discussion

Chemical composition of essential oils

Garden thyme (*Thymus vulgaris* L.).

The moisture of the plants was determined as 82.75%±0.80. The yield of essential oil was 0.56%±0.00 (in abs. dry mass was 3.26%±0.03). The oil was light yellow liquid with a characteristic, spicy-phenolic odor (Table 1). The oil is consisted by 35 components, representing 98.89% of the total content. Twelve of them were in concentrations over 1% and the rest 23 constituents were in concentrations under 1%. The major constituents (up 3%) of the oil were as follows: thymol (37.90%), *γ*-terpinene (19.44%), *p*-cymene (8.84%), *δ*-2-carene (3.92%), carvacrol (3.60%), and *β*-caryophyllene (3.37%). The results indicated that Bulgarian essential oil obtained from *T. vulgaris* is from thymol chemotype [19], which may also have a profound influence on its bioactivity, flavor, and aroma profile.

Table 1

Chemical composition of essential oil of garden thyme, rosemary, spearmint, sweet basil

№	Compounds	RI	Content, %			
			Garden thyme	Rosemary	Spearmint	Sweet basil
1	Tricyclene	922	-*	0.42±0.00	-	-
2	*α*-Pinene	939	2.39±0.02	13.37±0.12	1.31±0.01	0.56±0.00
3	Camphene	954	0.33±0.00	7.22±0.07	0.27±0.00	0.10±0.00
4	Sabinene	969	0.26±0.00	0.10±0.00	0.86±0.00	0.48±0.00
5	*β*-Pinene	979	0.37±0.00	2.37±0.02	1.24±0.01	0.79±0.00
6	Octen-3-ol	982	2.81±0.02	-	-	-
7	*β*-Myrcene	991	2.22±0.02	1.81±0.01	1.63±0.01	0.89±0.00
8	*α*-Phellandrene	996	-	4.27±0.04	-	-
9	*δ*-2-Carene	998	3.92±0.03	2.13±0.02	-	-
10	*α*-Terpinene	1018	-	-	0.24±0.00	-
11	*p*-Cymene	1025	8.84±0.08	-	-	-
12	Limonene	1030	0.54±0.00	-	13.90±0.12	0.33±0.00
13	Eucalyptol	1032	0.24±0.00	19.89±0.18	0.99±0.00	8.26±0.08
14	*cis-β*-Ocimene	1040	-	0.15±0.00	-	1.48±0.01
15	2-Phenylethanal	1047	-	0.10±0.00	-	-
16	*trans-β*-Ocimene	1050	0.36±0.00	0.13±0.00	0.20±0.00	0.13±0.00
17	*γ*-Terpinene	1055	19.44±0.18	2.26±0.02	0.46±0.00	0.28±0.00
18	*α*-Terpinolene	1088	-	1.81±0.01	0.38±0.00	-
19	*β*-Linalool	1092	2.59±0.02	0.96±0.00	0.53±0.00	30.52±0.29
20	*p*-Mentha-3-one	1131	-	-	0.87±0.00	-
21	(+)-Camphor	1126	-	16.86±0.16	-	0.33±0.00
22	*trans*-Menthone	1136	-	-	1.11±0.01	-
23	Pinocarvone	1157	-	0.67±0.00	-	-
24	Isomenthol	1158	-	-	0.30±0.00	-
25	Terpinen-4-ol	1163	-	-	-	0.90±0.00
26	(-)-Menthol	1164	-	-	0.84±0.00	-
27	Borneol	1169	1.65±0.01	5.27±0.05	-	-
28	(+)-Menthol	1168	-	-	1.29±0.01	
29	Terpinene-4-ol	1179	0.71±0.00	2.20±0.02	-	-
30	Methylchavicol	1186	-	-	-	13.16±0.12
31	Piperitol	1196	-	0.38±0.00	-	-
32	Dihydrocarvone	1204	-	-	3.37±0.03	-
33	cis-Carveol	1208	-	-	0.34±0.00	-
34	*α*-Terpineol	1189	0.37±0.00	4.10±0.04	-	1.07±0.01
35	Verbenone	1193	-	3.69±0.03	-	-

Table 1 (Continue)

Chemical composition of essential oil of garden thyme, rosemary, spearmint, sweet basil

№	Compounds	RI	Content, %			
			Garden thyme	Rosemary	Spearmint	Sweet basil
36	*β*-Citral	1215	0.13±0.00	-	-	-
37	Pulegone	1216	-	-	0.87±0.00	-
38	(-)-Carvone	1218	-	-	50.23±0.49	-
39	Piperitone	1228	-	0.25±0.00	-	-
40	Thymol methyl ether	1229	0.98±0.00	-	-	-
41	*p*-Menth-1-en-3-one	1231	-	-	2.22±0.02	-
42	Thymoquinone	1260	0.22±0.00	-	-	-
43	Isomenthyl acetate	1282	-	-	0.79±0.00	-
44	Thymol	1290	37.90±0.36	-	-	-
45	Bornyl acetate	1285	-	3.37±0.03	-	0.51±0.00
46	Carvacrol	1292	3.60±0.03	-	-	-
47	Eugenol	1337	0.51±0.05	0.41±0.00	-	11.74±0.09
48	*cis*-Carvyl acetate	1344	-	-	1.11±0.01	-
49	*trans*-Carveyl acetate	1365	-	-	0.25±0.00	-
50	Methyleugenol	1371	0.11±0.00	0.53±0.00	-	-
51	*β*-Bourbonene	1388	-	-	1.21±0.01	-
52	*β*-Elemene	1391	-	-	0.47±0.00	2.28±0.02
53	*β*-Caryophyllene	1419	3.37±0.03	1.20±0.01	2.77±0.02	0.42±0.00
54	*α*-Bergamotene	1426	-	-	-	6.36±0.06
55	*β*-Cubebene	1429	1.42±0.01	0.14±	2.65±0.02	-
56	*γ*-Elemene	1433	-	-	0.83±0.00	-
57	*δ*-Elemene	1435	0.30±0.00	-	-	-
58	*β*-Elemene	1451	0.29±0.00	-	-	-
59	*α*-Humulene	1454	-	-	0.38±0.00	0.85±0.00
60	*α*-Caryophyllene	1454	0.60±0.00	0.23±0.00	-	-
61	*γ*-Muurolene	1483	-	-	-	4.33±0.04
62	Bicyclogermacrene	1499	-	-	1.26±0.01	-
63	*β*-Bisabolene	1501	0.23±0.00	-	-	-
64	*α*-Bulnesene	1507			-	2.00±0.02
65	*γ*-Cadinene	1513	0.33±0.00	-	-	1.52±0.01
66	*δ*-Cadinene	1523	-	-	0.64±0.00	-
67	*δ*-Cadinene	1524	0.27±0.00	-	-	-
68	(-)-Spathulenol	1572	-	-	0.32±0.00	-
69	Germacrene D-4-ol	1570	0.51±0.00	-	-	-
70	Ledene oxide	1578	-	-	0.45±0.00	-

Table 1 (Continue)
Chemical composition of essential oil of garden thyme, rosemary, spearmint, sweet basil

№	Compounds	RI	Content, %			
			Garden thyme	Rosemary	Spearmint	Sweet basil
71	Caryophyllene oxide	1580	0.47±0.00	0.74±0.00	0.56±0.00	-
72	Germacrene D	1580	-	0.19±0.00	-	-
73	Cubenol<1,10-di-epi->	1618	-	-	0.29±0.00	-
74	*δ*-Cadinol	1619	-	0.66±0.00	0.61±0.00	1.92±0.01
75	*τ*-Cadinol	1634	-	0.73±0.00	0.52±0.00	1.07±0.01
76	*α*-Cadinol	1641	-	0.40±0.00	0.39±0.00	6.53±0.06
77	Phytol	2105	0.29±0.00	-	-	-
78	Squalene	2817	0.32±0.00	-	-	-

*- not identified

The moisture of the rosemary sample was 64.00%±0.60. The yield of essential oil was 1.09%±0.01 (in abs. dry mass was 3.03%±0.03). The oil was light yellow liquid with a characteristic, refreshing, pleasant odor. The oil is composed by 34 components (Table 1) representing 99.00% of the total content. Sixteen of them were in concentrations over 1% and the rest 18 constituents were in concentrations under 1%. It is obvious that the major constituents (up 3%) of the oil were as follows: 1,8-cineole (19.89%), (+)-camphor (16.86%), *α*-pinene (13.37%), camphene (7.22%), borneol (5.27%), *α*-phellandrene (4.27%), *α*-terpineol (4.10%), verbenone (3.69%), and bornyl acetate (3.37%). One of the values of aromatic components in the composition of the essential oil of rosemary is comparable to those obtained by De Mastro et al. [14]. The results indicated that Bulgarian essential oil obtained from *R. officinalis* is from camphor chemotype [19]. The differences in chemical composition were explained with the different extraction methodologies used.

The moisture of the spearmint sample was 84.60%±0.81. The yield of essential oil was 0.83%±0.00 (in abs. dry mass was 5.41%±0.05). The oil was light yellow liquid with a fresh, caraway-minty odor (Table 1). The results show that 40 components representing 98.95% of the total content were identified in the oil. Fourteen of them were in concentrations over 1% and the rest 26 constituents were in concentrations under 1%. It is clear that the major constituents (up 3%) of the oil were as follows: (-) carvone (50.23%) and limonene (13.90%), that qualitative and quantitative results are comparable with that identified from Nikšić et al. [31]. Through aromatic compounds isolated from *M. spicata* in Bulgaria, the carvone/limonene chemotype of the tested sample was established [19].

The moisture content of the sweet basil sample was 88.71%±0.86. The yield of essential oil was 0.19%±0.00 (in abs. dry mass was 1.70%±0.01). The oil was light yellow liquid with typical fresh-spicy odor. Results presented on Table 1 show that the tested oil was consisted of 27 components, representing 98.81% of the total content. Fourteen of them were in concentrations over 1% and the rest 13 constituents were in concentrations under 1%. As seen the major constituents (up 3%) of the oil were as follows: *β*-linalool (30.52%), methylchavicol (13.16%), eugenol (11.74%), 1,8-cineole (8.26%), *α*-cadinol (6.53%), *α*-bergamotene (6.36%), and *γ*-muurolene (4.33%), comparable to results obtained from other researchers [10]. The results indicated that Bulgarian essential oil obtained from sweet basil is a linalool chemo type [19].

The classification of the identified compounds, based on functional groups, is summarized in Figure 1. The predominant participation of oxidized monoterpenes in the essential oil of spearmint, rosemary and sweet basil is established.

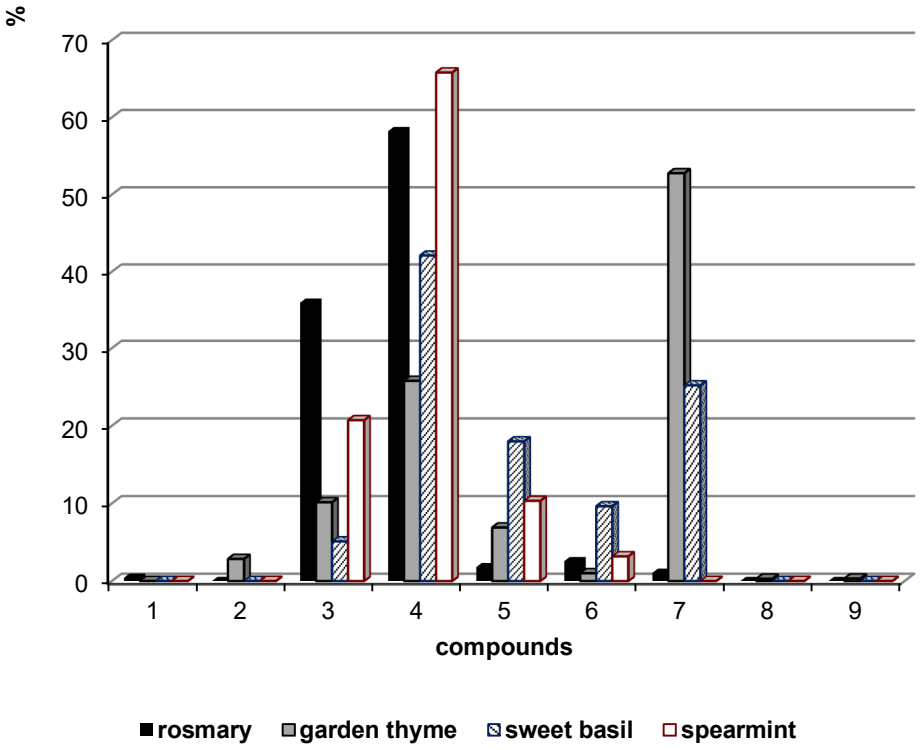

Figure 1. Group of components in essential oils from Lamiaceae, %,:
1-hydrocarbons,
2-oxygenated hydrocarbons,
3-monoterpene hydrocarbons;
4-oxygenated monoterpenes;
5-sesquiterpene hydrocarbons,
6-oxygenated sesquiterpenes,
7-phenylpropanoids;
8-diterpenes;
9-triterpenes.

Two groups of compounds were dominant in rosemary essential oil (Fig. 1), as oxygenated monoterpenes (58.21%) and monoterpene hydrocarbons (35.98%), followed by oxygenated sesquiterpenes (2.56%), sesquiterpene hydrocarbons (1.78%), and phenylpropanoids (1.05%).

Compounds, identified in garden thyme essential oil (Fig. 1) were phenylpropanoids (52.75%), ogygenated monoterpenes (25.78%), monoterpene hydrocarbons (10.14%), sesquiterpene hydrocarbons (6.89%), oxygenated hydrocarbons (2.84%), ogygensesquiterpenes (0.99%), triterpenes (0.32%), and diterpenes (0.29%).

Duke [16] summarized that the major aromatic components derived from the essential oil of *T. vulgaris* were as follows: thymol (23-60%), γ-terpinene (18-50%), p-cymene (8-44%) carvacrol (2-8%), and linalool (3-4%). The reason for the different results may be caused by the origin of the sample, environmental differences, age of the plant, dissimilarities in method of isolation and seasonality.

Oxygenated monoterpenes (42.09%), phenylpropanoids (25.20%), and sesquiterpene hydrocarbons (17.98%) were the dominant group in sweet basil essential oil (Fig. 1), followed by oxygenated sesquiterpenes (9.63%), and oxygenated hydrocarbons (5.10%).

Oxygenated monoterpenes (65.80%) were the dominant group in spearmint essential oil, followed by monoterpene hydrocarbons (20.71%), sesquiterpene hydrocarbons (10.32%), and phenylpropanoids (3.17%).

The differences in the quantitative and qualitative composition of essential oils of garden thyme, rosemary, spearmint and sweet basil and their aromatic components in relation to the previous researches may be probably due to different environmental and genetic factors, different chemotypes and the nutritional status of the plants as well as other factors that can influence the oil composition.

Antibacterial activity

The results of antibacterial testing are presented in Table 2.

All essential oils showed good antibacterial potential against tested four strains of foodborne pathogens. *E.coli* was the most susceptible bacterium strain. The essential oils of spearmint and rosemary possessed the most pronounced antibacterial activities against *E. coli* (with inhibition zone: 32.00 mm and 30.00 mm). Garden thyme was most effective against *E. coli* due to the two major constituents as thymol and carvacrol, because of their ability to break the outer membrane of Gram-negative bacteria and increase the permeability of the cytoplasmic membrane. On the other hand, the essential oil of sweet basil showed highest antibacterial property against *S. enterica* owing to the presence of the major compound linalool.

The weakest potential was observed by the spearmint oil against *S. enterica.* All these spices, widely used in culinary technology contain compounds that have been shown to possess antibacterial functions. Studies have shown that constituents with a phenolic structure in essential oils, such as eugenol, carvacrol and thymol have the greatest antibacterial activities, followed by aldehydes, ketones, alcohols, ethers and hydrocarbons [39, 24].

Table 2

Diameter of zones of growth inhibition (mm) of tested pathogenic bacteria

Bacteria / Sample	*E. coli* ATCC 8739	*S. enterica* NCTC 6017	*L. monocytogenes* NCTC 11994	*S. aureus* ATCC 25093
	Zones of growth inhibition (mm)			
Garden thyme	21.01±0.20	12.02±0.11	19.01±0.18	20.03±0.19
Rosemary	30.04±0.28	11.01±0.10	13.02±0.12	11.01±0.10
Spearmint	32.00±0.30	12.00±0.11	6.00±0.05	11.02±0.10
Sweet basil	17.01±0.16	20.03±0.19	7.02±0.06	15.02±0.14

Our results for garden thyme were in agreement with the findings of El Hattabi et al. [17].

The results of the antibacterial activity of the spearmint essential oil were lower than the findings of Horváth and Koščová [23] reported the highest antibacterial properties against *S. aureus* CCM 4223 with inhibition zone varied at a range of 35.67 mm. The results obtained in this study are comparable to the findings of Moghaddam et al. [30, 37] reported that sweet basil essenatial oil showed inhibition zones against *S. aureus* (29.20–30.56 mm), and *E. coli* (17.48-23.58 mm).

Differences in the geographic environment, the cultivar type, age of the plant, different methods of isolation, and seasonality of the samples could be the reasons for the obtained differences in spectrum of antibacterial activity.

Conclusion

In the present study the aromatic composition and antibacterial properties of essential oils of thyme, rosemary, spearmint, and sweet basil were investigated. The results show the presence of alcohols and ketones in the aromatic composition of the essential oil. The identified aromatic compounds exhibit antimicrobial properties against foodborne pathogens. The essential oil of garden thyme possessed the strongest antimicrobial activity against *S. aureus* and *L. monocytogenes.* Otherwise, essential oil of sweet basil showed most pronounced antimicrobial properties against *S. enterica*, while *E. coli* was most susceptible to the essential oil of spearmint and rosemary. The results obtained provide a basis for a thorough examination of the chemical composition and antimicrobial properties of various representatives of Lamiaceae family with a view to a wide usage in food technology.

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Cryoprotective ability of starch syrup in the composition of aromatic and fruit-berry ice cream

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Abstract

Introduction. The purpose of the research is to study the influence of starch syrup of various carbohydrate composition and its compositional mixtures on the formation of physico-chemical indicators of ice cream on the basis of sugar syrups.

Materials and methods. As a substitute of sugar for ice-cream was used starch syrup with different functional and technological properties – syrup caramel low-saccharification (SC) and glucose-fructose syrup (GFS) with a dry matter content of at least 78%. The cryoscopic temperature was determined using Beckmann's thermometer, the content of frozen water was calculated in accordance with the obtained values of the cryoscopic temperature, the microstructure was investigated using a light microscope with a cooling chamber for increasing x400 and x600.

Results and discussion. For complete replacement of sugar in the ice cream the starch syrup of different degree of saccharinization was chosen: glucose-fructose syrup GFS (dextrose equivalent 98) and syrup caramel SC (dextrose equivalent 30). GFS, in comparison with control samples with sugar, due to the high content of mono-sugars, significantly reduces the cryoscopic temperature of the mixtures. While, the SC boosts this figure. Therefore, in order to maintain the recommended balance on the content of frozen water at each stage of low-temperature processing of ice cream mixtures, it is expedient to combine the cryoprotective capacity of the syrup with different dextrose equivalent. The ranges of optimal correlations between GFS and SC in compositions were calculated, allowing to receive the content of frozen water, according to control samples – from 30:70 to 40:60 for aromatic ice cream and from 50:50 to 90:10 – for fruit-berry ice-cream. Microstructural analysis of ice cream samples has demonstrated the expediency of complete replacement of sugar on the syrup compositions, which provides the formation of a more homogeneous finished product structure, compared with control samples with sugar.

Conclusions. The cryoscopic temperature of the mixtures, the content of the frozen water, and the size of the particles of the disperse ice cream systems can be adjusted by the use of starch syrup compositions with different dextrose equivalent.

Introduction

Cryoscopic temperature (t_{cr}) of mixtures for production of ice-cream is one of the main physical characteristics that determine the nature of the process of cooling the water during freezing, hardening and storage of the finished product [1]. The resulting crystals of ice are unstable in time and can be detected due to disturbances in the temperature regimes of production and storage [1, 2].

Exactly the content of the chemical and physical-chemical bound water in the mixture for ice cream production affects on t_{cr} that causes the crystallization process and the size of the crystals in the finished product [3]. Low molecularity, truly soluble in water compounds-sucrose, lactose and salt reveal the best effect on the tcr of ice cream mixtures [4]. The role of proteins and polysaccharides in this process is mediated and manifested through the connection of water, which cannot be solvent, which leads to increase of concentration of solutions of simpleand double sugar, salts in the residual of free water [5, 6, 7].

The cryoscopic temperature of ice-cream mixtures, depends not only from the number of dissolved molecules, but also from their molecular weight. Substances of lower molecular weight exhibit greater cryoprotective capacity [8]. Therefore,simple sugars, compared with double sugars, have a greater influence on tcr of aqueous solutions [9].

Except for less cryoprotective ability of double sugars, they are able to intensively crystallize during storage with the formation of large crystal sizes (≤ 10 microns) and their subsequent accretion [10, 11].

A special place in the market for frozen desserts is ice cream based on sugar syrups, which do not have milk components [12]. Within certain species of such ice cream there are certain requirements for the content of sweeteners, in particular, white crystalline sugar [13]. Thus, the content of sugar in aromatic ice-cream and fruit-berry is in the range of 20-22 to 30-32%. It is sugar that traditionally performs the function of an intensive sweetener and a source of dry matter, the proportion of which is based on their total content in aromatic and fruit-flavored ice cream of about 80-90%. Due to lower solubility, double sugars can form large crystals in ice-cream based on sugar syrups during its long-term storage. In order to prevent the appearance of a hard sugar chop on the surface of portions, sugar in this ice cream is recommended to replace on starch syrup, invert sugar or monosaccharin [14, 15, 16] by 20-25%. At the same time, starch syrup is the best alternate way thank to its price, safety indicators and functional-technological characteristics. Particular attention deserves polyfunctional technological properties of syrup of varying degrees of assessment, which are capable of amplifying, structuring ice cream and detecting cryoprotective ability [17, 18].

The authors for the first time have proved the expediency of a complete replacement of sugar in ice cream with milk base on syrup and its compositions. In the case of combination of high and low-sugar syrup, the degree of sweetness, the resistance to dampness, the aqueous phase, viscosity and the size of ice crystals and bubbles of the air are regulated [19, 20]. But especially important is the study of the process of freezing water in ice cream on the basis of sugar syrups – aromatic and fruit-berry. At the same time, information on the influence of starch syrup on the physico-chemical characteristics of ice cream in this group is absent.

The purpose of scientific research is to study the influence of starch syrup of various carbohydrate composition and its compositional mixtures on the formation of physico-chemical indicators of ice cream on the basis of sugar syrups.

The research objectives are as follows:

- to study the cryoprotective ability of starch syrup with low and high dextrose equivalent and the possibility of combining the syrup in aromatic and fruit-berry ice cream with complete replacement of sugar;

- to optimize the composition of carbohydrate complexes for the complete replacement of sugar in ice cream on the basis of the analysis of the patterns of freezing of water in mixtures for the production of ice cream;
- to find out the degree of influence of separate stages of low-temperature processing of mixtures with different carbohydrate composition on the content of frozen water;
- to confirm the efficiency of replacing sugar in the compositions of syrup by means of microstructural analysis.

Materials and methods

Materials

As a substitute of sugar for ice-cream was used starch syrup with different functional and technological properties – syrup caramel low-saccharification (SC) and glucose-fructose syrup (GFS) with a dry matter content of at least 78% (Table 1).

Table 1

Sensory attributes and physico-chemical properties of glucose syrup with different degree of starch conversion [12, 13].

Indicator	Syrup Caramel (SC)	Glucose-fructose syrup (GFS)
Organoleptic characteristics	Homogeneous, very viscous, colorless liquid. The taste is moderately sweet, without any foreign taste and smell.	Homogeneous, liquid with yellowish color. The taste is over sweet, without any foreign taste and smell
Dextrose equivalent (DE)	30	98
Mass fraction of glucose,%	10	54
Mass fraction of maltose,%	20	2
Mass fraction of maltotriosis,%	absent	1
Mass fraction of higher sugars,%	70	1
Mass fraction of fructose,%	absent	42
Profile of sweetness	30	98

The recipe composition of the experimental samples was developed in accordance with a typical mixtures composition of a wide assortment range [19]:

- aromatic ice cream (mass fraction of dry matter – 20,5-26,5%, including sugar 20-26%, citric acid – 0,2%, stabilization system Kremodan ® DC – 0,3%);
- fruit-berry ice cream (a mass fraction of dry substances – 25-35%, including sugar 22-32%, a mass fraction of dry matter of fruits and berries – 2.7%, the content of stabilizing system Cremodan ® DC – 0.3%).

For control 1 samples of ice cream with a minimum sugar content (aromatic – 20%, fruit-berry – 22%) were selected.

For control 2 – samples of ice cream with the maximum content of sugar (aromatic – sugar 26%, fruit and berry – 32%)

In the experimental samples, the mass fraction of dry matter of GFS and PCs and their composition mixtures (for the ratio between syrup from 10:90 to 90:10) is selected according to the most popular formulations within the permitted range of sugar contents, namely:

– 25% – for aromatic ice cream;

– 27% – for fruit-berry ice cream.

Contain a mass fraction of SS solids in the composition of GFS + PS in amounts of 100, 80, 60, 40, 20 and 0% respectively (samples 1-6).

Ice cream mixtures were pasteurized at 85 ± 2 ºC for 2-3 minutes, cooled to 4 ± 2 ºC and maintained at this temperature for 2 hours [20].

Experimental ice-cream production was carried out on the frizer of the periodic action of the brand "Fibre-400", FPM-3,5 / 380-50. The investigated ice cream samples were hardened and stored in a freezer "Caravell" A / S at a temperature of minus 18-20 °C [19, 20].

Methods

The research was conducted in the following sequence:

- determined the cryoprotective capacity of caramel syrup and glucose-fructose syrup, as well as their compositions, by measuring the cryoscopic temperature of mixtures of aromatic and fruit-berries;
- studied the dynamics of freezing of free water during technologically significant stages of low-temperature processing of mixtures with different carbohydrate composition using two-factor regression analysis of experimental data;
- confirmed the expediency of using compositions of syrups by analyzing the microstructure and the external type of ice cream samples.

Cryoscopic temperature. The cryoscopic temperature of ice cream mixtures was determined using cryostat and Beckmann thermometer (TL-1) [15, 21].

The amount of frozen moisture. The amount of frozen moisture at different temperature regimes for non-dissociated molecular solutions was calculated according to the formula [15, 22]:

$$\omega = [1 - (t_{cr} / t)] \cdot 100$$

where ω – number of frozen water,%;

t – temperature, ºC.

Microstructural analysis. The microstructural analysis of the ice cream was carried out using a light microscope of the brand XS-2610 with a cooling chamber with an increase of x400 and x600. The sizes of air bubbles and ice crystals of ice cream samples were determined using a graduated eyepiece grid [15].

The results of the triple repetition study were processed by the method of mathematical and statistical processing at a given confidence probability $P \geq 0.95$.

Results and discussion

Determination of the cryoprotective ability of syrups

At the first stage of the work, the cryoscopic temperature of the samples of aromatic and fruit-berry ice cream of traditional composition with sugar and ice cream with complete replacement of sugar to syrup GFS and SC and their compositions (Figure 1).

According to Figure 1, the substitution of sugar to caramel syrup SC with a low dextrose equivalent does not allow to decrease the cryopreservation temperature to the significance of the traditional types of ice cream. Consequence of high values of t_{cr} can become excessive freezing of free water with the creation of a coarse-crystalline structure. In the case of the use of only GFS, the reduction of t_{cr} is very important that can only be taken for the production of soft ice cream and ice cream-soufflé. Therefore, it is obvious to combine high-sugar syrup with syrup of low DE at ratios, ranges of values that need to be clarified [19, 20].

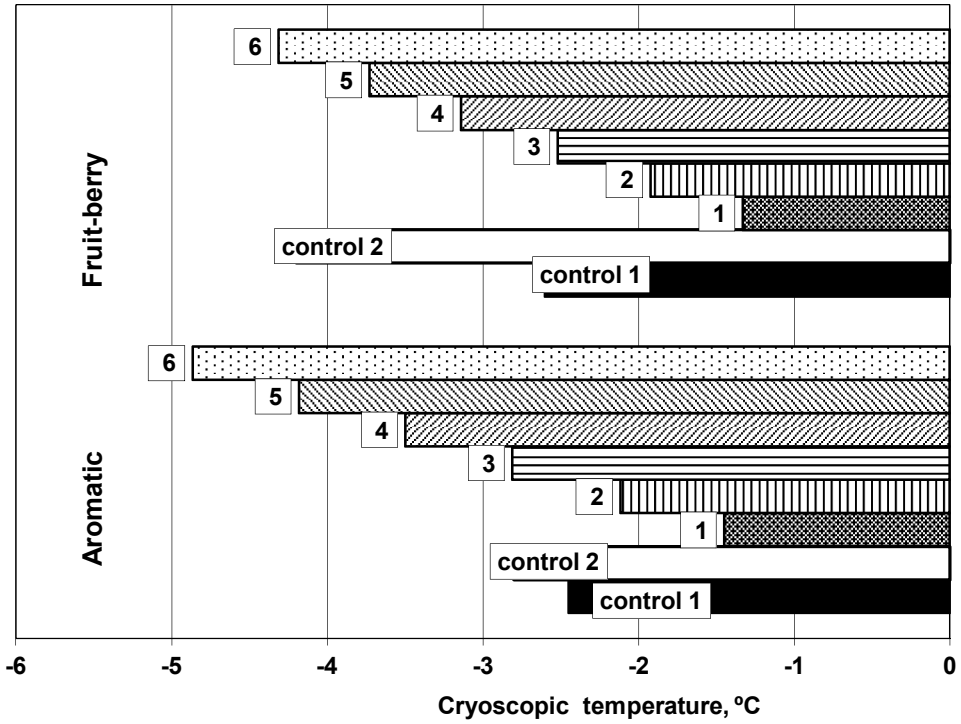

Figure 1. Cryoscopic temperature of ice cream samples with sugar and ice cream with complete replacement of sugar on GFS and PC ***Legend:***

- **control 1 –** samples of ice cream with a minimum sugar content (aromatic – 20%, fruit-berry – 22%);
- **control 2 –** samples of ice cream with the maximum content of sugar (aromatic – 26%, fruit-berry – 32%)
- **samples 1-6:** contain a mass fraction of SS solids in the composition of GFS + PS in amounts of 100, 80, 60, 40, 20 and 0% respectively

Study of free water freezing process

For this purpose, based on the established values of cryoscopic temperatures (Figure 1), the content of frozen water in ice cream was calculated at technologically significant stages of low-temperature processing [22]:

- №1 – freezing (minus 6 ºC);
- №2 – temporary storage of ice cream (minus 12 ºC);
- №3 – storage of ice cream for a duration of up to 10 months (minus 18 ºC);
- №4 – storage of ice cream for a period of up to 12 months (minus 24 ºC);
- № 5 – hardening of ice cream in a continuous way (minus 30 ºC);
- №6 – hardening of ice cream in a continuous way (minus 40 ºC).

Figure 2 shows graphic 3D models that demonstrate the dynamics of water freezing at individual stages of the technological process, for the aromatic and fruit-berry ice cream obtained by the two-dimensional approximation method.

Two-dimensional approximation of the technological process made possible to study the process as a whole and at each stage separately by replacing the experimentally determined plane with an approximating one. The calculation error is $\varepsilon = 0.05\%$.

Figure 2 shows graphical 3D models that demonstrate the dynamics of water freezing at individual stages of the process for aromatic and fruit-berry ice cream.

On the plane XZ (Figure 2), are shown recommended ranges of dry matter content of low-sugar syrup in GFS + PC compositions, which satisfy the requirements for the content of frozen water for control samples of traditional composition with white crystalline sugar, are singled out. According to Figure 1, ranges of values of tcr for control samples of aromatic ice cream for a minimum (20%) and a maximum (25%) content of sugar are in the range from minus 2.45 °C to minus 2.80 °C. For control samples of fruit and berry ice cream for the minimum (22%) and maximum (32%) sugar content, the fluctuations of values are higher and range from minus 2.6 to minus 4.2 °C.

Taking into account this, the ranges of allowable values of frozen water in the studied samples of ice cream at the individual stages of the technological process are calculated. This made it possible to identify the rational content of low-sugar syrup PC in the GFS + PC complex for aromatic ice cream (PC = 60–70%) and for fruit-berry ice cream (PC = 10–50%) and to isolate these ranges of values in Figure 2

From Figure 2 shows the different character of freezing of water for aromatic and fruit-berry ice cream . Increased content of sugars in the fruit-berry ice cream makes it more effective to freeze water. At stage 1 (freezing) in aromatic ice cream during to recommended composition of the syrups, from 23 to 30% of water are frozen, and in fruit-berry – up to 25–43%. Further hardening on 2nd stage increases the content of frozen water in these types of ice cream to 68–70% and 69–76%, and at stages 5 and 6 – up to 91 and 93%, respectively. Therefore, it should be noted that the most important role of the stages of freezing and tempering ice cream in the technological cycle of its production. Therefore, observance of the recommended low-temperature processing techniques in ice cream technology with high content of sugars is an extremely important condition for the guaranteed quality of the product.

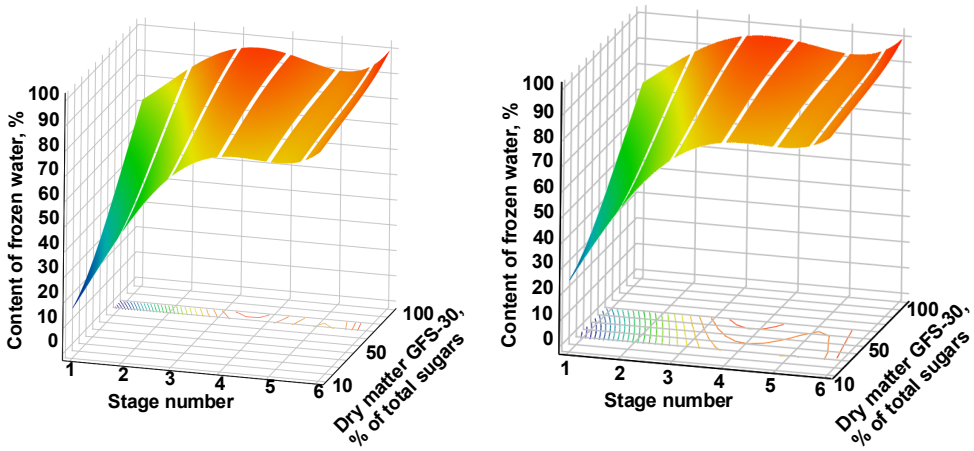

Figure 2. Graphic 3D models of water freezing dynamics at individual stages of the technological process for aromatic (a) and fruit-berry (b) ice cream

Research of microstructural analysis of ice cream

To further confirm the appropriateness of the complete replacement of sugar in ice cream, a comparative analysis of the microstructure of control samples with sugar and samples with complete replacement of sugars was carried out on compositions of syrups [20].

For ice cream, the aromatic ratio between the GFS and the PS was chosen within the optimal range of 40:60 (25% by weight of sugars), and for fruit and berry ice cream – 60:40 (mass fraction of sugars – 27%). Ice cream samples were subjected to low-temperature processing – hardening at a temperature of minus 30 ºC and storage at a temperature of minus 18 ºC for 1 month.

To illustrate the effect of higher structuring sugars and cryoprotectants-monosugars in the composition of the PS on the size of air bubbles and ice crystals, microphotographs of ice cream samples of classical and improved composition are presented (Figure 3). From the given microphotographs, it is evident that the syrup have a significant influence on the size of the disperse particles, especially in the case of a complete replacement of sugar in the aromatic ice cream composition of the GFS composition: PS = 40:60. The maximum size of air bubbles in ice cream dropped from 95 microns to 67 microns, and crystals of ice – from 60 microns to 39 microns.

A slightly less influence on the degree of dispersion of the air phase was observed for fruit-berry ice cream, the maximum size of air bubbles which decreased from 72 microns to 59 microns, and crystals of ice – from 45 microns to 40 microns. The higher content of dry matter, in particular, the presence of plant origin polysaccharides, contributed to a better distribution of air in ice cream and in addition to counteract the growth of ice crystals [2, 3, 10].

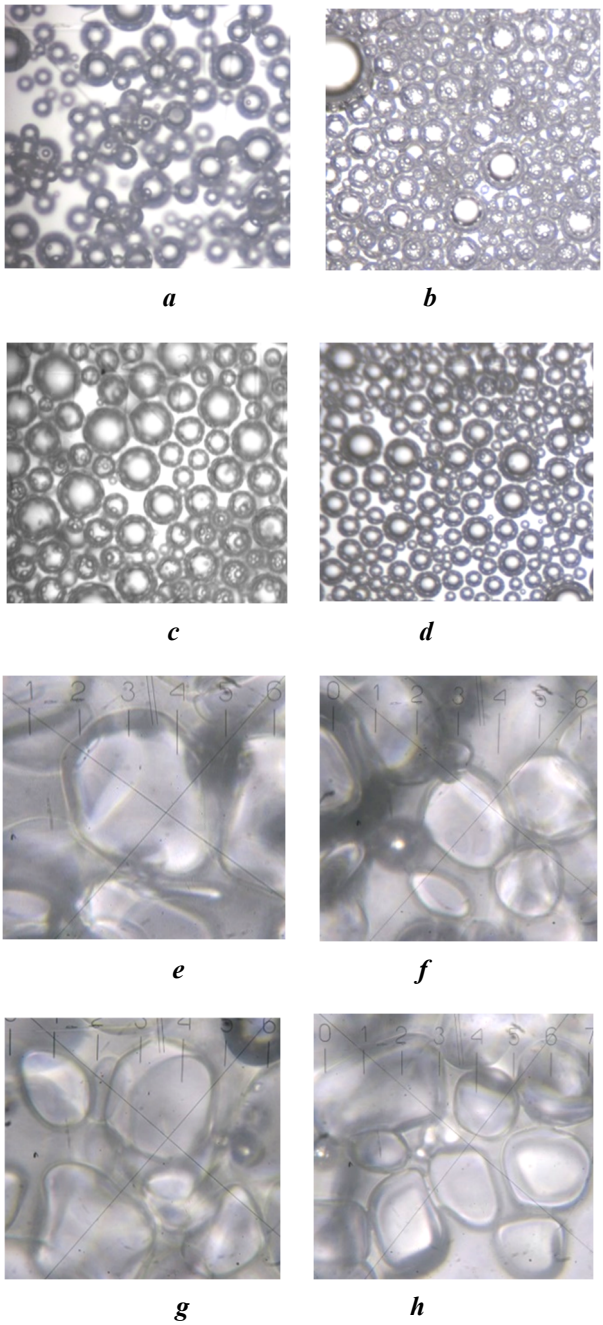

Figure 3. Air bubbles and ice crystals of aromatic ice cream with sugar (a, b) and syrup (g) and fruit-berry ice cream with sugar (e, f) and syrup (g, h)

In composition of such samples, the syrup with a high dextrose equivalence actively binds water and detects cryoprotective effect. Also low-sugar syrup structures water phase, stabilizing the air bubbles and mechanically counteract the excessive growth of water crystals. The obtained results correlate with the well-known scientifically proven recommendations regarding the expediency of a partial replacement of sugar to corn syrup [10, 11, 23]. At the same time, for the first time, the authors established the polyfunctional action of syrup in the formation of a wide range of physico-chemical characteristics, and scientifically achieved combinations of this sweetener with a different dextrose equivalent during to complete replacement of sugar in the composition of the finished product.

The prospect of further research is to carry out a research analysis of the technological role of starch in composition of ice cream on milk base and without milk components.

Conclusions

1. The cryoscopic temperature of mixtures for the production of ice cream can be adjusted by the use of starch syrup with different dextrose equivalent. Depending on the content of monosaccharides, the syrup exhibits a different cryoprotective capacity.
2. For complete replacement of sugar in the composition of ice cream on a composition of glucose-fructose syrup (dextrose equivalent 98) and caramel syrup (dextrose equivalent of 30) for ratios of 30:70 to 40:60 for aromatic ice cream and from 50:50 to 90: 10 for fruit-berry ice cream , in the ice cream at all stages of the technological process the nature of freezing of free water is similar to the samples of the classical chemical composition.
3. Composite mixtures of syrup have a comprehensive effect on the formation of disperse ice cream systems.

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Bioactivity of Algerian palm dates *Phoenix dactylifera* L.

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Abstract

Introduction. The current study was conducted in order to evaluate *in vitro* the phytochemical profile and antibacterial activity of Algerian palm dates *Phoenix dactylifera L.*

Materials and methods. Qualitative and quantitative (total polyphenols, flavonoids and antioxidant activity)phytochemical analysis were performed on aqueous and methanolic extracts of seven varieties of dates as the evaluation of antibacterial activity against *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC 25922 strains.

Results and discussion. Phytochemical screening of aqueous and methanolic extracts showed the presence of several families of chemical compounds such as catechin tannins, saponins and terpenoids in the seven varieties of dates. The screening of these extracts reveals slight qualitative differences with a greater presence of saponins in the aqueous extract while terpenoids are present in large quantity in the methanolic extract. A quantitative characterization of extracts showed significantly high levels (P<0.05) in the methanolic extract from: 85.8±0.8 to 275 ± 0.07 GAE/100g, 36.9 ± 0.3 to 70.1 ± 0.9 QE/100g and 18.5 ± 0.9 to 58.5 ± 0.5% vs. 66.1±0.2 to 189±0.09 GAE/100g, 29.1±0.5 to 50.8±0.6 QE/100g and 14.7±0.4 to 41±0.1% in aqueous extracts for total polyphenols, flavonoids and reducing power respectively. The susceptibility of bacterial species to various extracts of *Phoenix dactylifera* L. fruits by agar well diffusion assay showed a maximum inhibition zone diameter (IZD) of 43.0 ± 1.0 and 26.3 ± 1.5 mm for the methanolic extract of the variety *Tamesrit* against *S. aureus* and *E. coli* strains respectively. The minimum inhibitory concentrations (MIC) ranged from 0.08 g / mL for the methanolic extract of the variety *H'mira* against *E. coli* to less than 0.04 g/mL for the methanolic extracts of the varieties *Tamesrit, Akerbouch* and *Bent Kbala* against *S. aureus.*

Conclusion. Given the interesting contents of polyphenols, flavonoids and antioxidant activity in addition to the inhibitory power of date extracts, we can conclude that this product could be an excellent source of antioxidants and bioconservatives in food preparation.

Introduction

The use of antibiotics is currently contested due in part to their high costs and potential toxicological risks and on the other hand, their frequent consumption could lead to resistance of strains and be responsible for therapeutic failures [1, 2]. Secondary metabolites are natural plant compounds, available at low cost. Due to their natural antioxidant and antibacterial effects, they can constitute pharmacological alternatives for the prevention and the treatment of several pathologies [3, 4]. For thousands of years, dates, fruits of *Phoenix dactylifera* L., are known to have many medicinal properties and in countries ranging from the Near East to the Middle East are used in traditional medicine as protectors and curatives [5-7]. Moreover, this fruit having many favorable biological properties as antioxidant, antimicrobial…. [8, 9]. In Algeria, the date occupies a very important place with an average annual production estimated at 1029596 tons; this allowed him to occupy the world's third largest producer of date [10]. But its valuation and exploitation as sources of natural bioactive substances endowed with antibacterial activity which presents an interest in the field of biopharmaceuticals are very limited. The objective of this study is to evaluate *in vitro* bioactivity of seven varieties of Algerian dates on phytochemical profile and antibacterial activity against two bacterial strains (*Staphylococcus aureus, Escherichia coli*) frequent in human pathology and often responsible for food poisoning.

Materials and methods

Plant material

Seven (07) date palm cultivars at the "*Tmar*" stage (maturity stage) locally known as: *H'mira, Adhem Fgig,BouzrourAkerbouch, Bentkbala, Ghars* and *Tamesrit* from the region of Ghardaia (southern Algeria) were used for the experimentation. 10 kg of each variety harvested (season 2017) in the same locality were provided by farmers. After cleaning, samples were placed in hermetic bags and stored at 4 °C until analysis.

Extract preparation

The pulps of each variety previously cleaned and ground, constitute the raw material for extracts. For aqueous extract, 10g of each variety are mixed with 100 mL of distilled water and continuous stirred for 2 h at room temperature then filtered. The methanolic extract is prepared by mixing 10g of pulps to 50 mL of methanol/water (80:20, V/V), placed under slow stirring for 24 h at room temperature then reduced under pressure in a rota-vapor to remove methanol.

Phytochemical analysis

Phytochemical analysis on aqueous and methanol/water extracts of dates was determined. Some phytochemical groups have been characterized, according to the methods described by Ciulei [11], tannins by the $FeCl_3$ test; alkaloids per Dragendorff reagent, the saponins per froth test, terpenoïds by Salkowski reaction (to 0.5 g of the extract were added to 2 ml of chloroform and 3 ml of concentrated sulfuric acid H_2SO_4 where a reddish-brown color indicates the presence of terpenoids) [12] and anthocyanins using HCl and NH_4OH test

[13]. The total phenolics contents were determined using Folin-Ciocalteau reagent according to Singleton and Rossi method [14] using gallic acid as standard. The results are expressed in mg of Gallic Acid Equivalent (GAE)/100g of fresh weight. The flavonoids amount is determined according to Lamaison and Carnat [15] method using quercitin as standard; the results are displayed in mg of Quercitin Equivalent /100g of fresh weight. The antioxidant activity is performed according to the FRAP method [16], the results obtained are expressed in mg of vitamin C per 100 g of the fresh fruit.

Antibacterial susceptibility assay

Bacterial strains. Two ATCC reference bacterial strains were used for the antibacterial susceptibility assay of different date extracts: *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC 25922 stored at -20 °C in glycerol.

Agar well diffusion assay and determination of MIC. The potential antibacterial activity of the aqueous and methanolic extracts of the pulp of the different cultivars was evaluated *in vitro* by the standard agar well diffusion assay [17]. From a culture of the bacterial suspension of 18 hours at 37°C, an inoculum adjusted to 0.5 Mac Farland density (a dilution of 1/10th and 1/100th of the bacterial suspension respectively of *S. aureus* and *E. coli* was performed in sterile distilled water before inoculation [18]) was seeded uniformly by tight streaks with a sterile cotton swab on the surface of the Petri dish (90 mm) containing 20 mL of Muller Hinton agar. Four wells/dish of 6 mm diameter each were perforated in the agar with the tip of a sterile Pasteur pipette and filled with 100 µL of aqueous or methanolic palm dates extracts (0.20 g/mL). All plates were incubated for 24 h at 37°C. The antibacterial activity is evaluated by measuring the diameter of the inhibition zone (IZD) formed around the well. The percentage of growth inhibition is calculated by the formula: I% = IZD/PDD*100 (IZD: Inhibition Zone Diameter, DD: Petri Dish Diameter=90mm) [19]. For assessment of minimum inhibitory concentration (MIC), the incorporation technique in agar is used [20] with some modifications. A concentration range of the aqueous and methanolic crude extracts was prepared respectively in water and methanol/water to have final concentrations of 0.04, 0.08, 0.12, 0.16 and 0.20 g/mL. 2 mL of each extract were incorporated in 18 mL of Muller Hinton agar maintained liquid and all is well stirred. After the agar plates completely solidified, 100 µL of the bacterial suspension already adjusted under the same conditions described above are inoculated by swabbing at the surface of the dish and all is incubated for 24 h at 37°C. The CMI is defined as the lowest concentration at which there is no visible growth [21]. The solvents used for the preparation of extracts (distilled water and methanol/water) are used as negative controls. While some antibiotics are used as positive controls to check their effects on the growth of each germ and are compared to the critical values of the diameters of

the zones of inhibition data by CA-SFM/EUCAST [22].These are: Tetracycline (30µg/disc), Ceftazidime (30µg/disc), Chloramphenicol (30µg/disc), Ampicillin (10µg/disc), Fosfomycin (200µg/disc), Cefazolin (30µg/disc) and Colistin sulfate (10µg/disc).

Statistical analysis

Each assay was carried out in triplicate. All experiments are expressed as mean ± standard deviation (SD). The data were treated using the STATISTICA software (Version 8) by the ANOVA test followed by the Duncan test for multiple comparisons.

Results and discussion

Phytochemical characterization of date extracts

Table 1

Phytochemical screening of aqueous and methanolic date extracts

Varieties	Saponins	Catechic tannins	Terpenoids	Anthocyans	Alkaloids
	Aqueous extract				
Ghars	+++	++	+	-	-
Tamesrit	+++	++	++	-	-
AdemFgig	+ + +	+	++	-	-
Akerbouch	+ + +	+ + +	+ +	-	-
BentKbala	+ + +	+ + +	+ +	-	-
Bouzror	++	+ + +	+ +	-	-
H'mira	+ +	+ + +	+ +	-	-
Methanolic extract					
Ghars	++	++	++	-	-
Tamesrit	++	++	+++	-	-
AdemFgig	+ +	+	++ +	-	-
Akerbouch	+ +	+ + +	+ + +	-	-
BentKbala	+ +	+ + +	+ + +	-	-
Bouzror	+	+ + +	+ + +	-	-
H'mira	+	+ + +	+ + +	-	-

+++ Very intense, ++ intense, + weak, − absent

Qualitative phytochemical analysis (Table 1) detected the presence of saponins, tannins and terpenoids in (methanolic/aqueous) date extracts.

The results depended on the reactions, going from clearly to weakly positive. These observations are similar to those reported by others authors indicating that *Phoenix dactylifera* fruit is a potential source of secondary metabolites [23-24]. A comparison of date extracts composition found that methanolic extracts presented greats levels of terpenoids than aqueous ones witch possessed more saponins, while both extracts had the same tannins contents. These results indicated the influence of the extraction solvent on the total content of secondary metabolites. Similar findings were obtained by others studies [25-27]. In contrast, anthocyans and alkaloids were absents in all date extracts.

Quantitative analysis of the composition on secondary metabolites showed a significant difference between the seven date cultivars extracts contents (Table 2). *Tamesrit* variety gave the highest levels of flavonoids and total polyphenols, followed by *Akerbouch* and *BentKbala* varieties thus reflecting interesting antioxidants activities with 58.5, 50.2 and 40.8% respectively. The aqueous extract revealed a low content of antioxidant compounds compared to the metanolic extract. Moreover, the antioxidant activity is inversely proportional to the richness in antioxidant compounds on the aqueous extract however, it seems to be more proportional to the flavonoids levels on the methanolic extracts; theses phytochemicals are a group of polyphenolic compounds, which have multiples pharmacological properties, they

presents strong antioxidant power [7] and could participate also in antibacterial activity [28-31].

Table 2

Polyphenols, flavonoids contents and antioxidant activity of aqueous and methanolic date extracts

Compounds / Varieties	Polyphenols (mg GAE/100g)	Flavonoids (mg QE/100g)	Antioxidant activity (%)
Aqueous extract			
Ghars	76.5±0.7^{d}	30.9±0.9^{e}	36.9±0.1^{b}
Tamesrit	189±0.09^{a}	46.7±0.3^{b}	14.7±0.4^{e}
Adhem Fgig	66.1±0.2^{e}	29.1±0.5^{f}	41±0.1^{a}
Akerbouch	123±1.1^{b}	50.8±0.6^{a}	16.4±0.8^{d}
Bent Kbala	121±0.9^{b}	36±0.7^{d}	17.8±0.7^{d}
Bouzrour	88.5±0.8^{c}	41±0.2^{c}	28.9±0.9^{c}
H'mira	89.2±0.6^{c}	31.2±0.1^{e}	29.7±1.2^{c}
Methanolic extract			
Ghars	103±1.1^{e}	41±0.3^{e}	21.3±1.3^{e}
Tamesrit	275±0.07^{a}	67.2±1.2^{a}	58.5±0.5^{a}
Adhem Fgig	85.8±0.8^{f}	36.9± 0.3^{f}	18.5±0.9^{f}
Akerbouch	173±0.6^{ab}	70.1±0.9^{a}	50.2±0.4^{b}
Bent Kbala	172±0.2^{b}	50±0.9^{c}	40.8±2.5^{c}
Bouzrour	117.5±0.5^{d}	55±1.0^{b}	36.2±0.9^{d}
H'mira	123 ± 1.1^{c}	44.3±0.9^{d}	23.7±0.3^{e}

The means followed by the letters a, b, c, d, e and f in the same column are significantly different ($p<0.05$).

3.2. Antibacterial activity of date extracts

The antibacterial activity of the aqueous and methanolic extracts of the seven date varieties against two pathogenic bacterial (*Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 25923) revealed that the aqueous extracts have not expressed inhibition zones around the wells, whereas methanolic extracts showed a strong antibacterial activity against the two bacterial strains. Our results are in a good concordance with some studies like [32-33]. The difference between the antibacterial activities could be explained by the nature and the concentration of the metabolites content in each type of extract. Indeed, the ability to extracting and solubilizing phytomolecules is very different and depends strongly on the solvent type [34-35]. According to Cowan [36], it could be deduced that the antibacterial substances contained in dates are more soluble in methanol.

Moreover, the active extracts were significantly more effective ($P<0.05$) on *S. aureus* (IZD: 15 to 43 mm) than on *E. coli* (IZD: 11 to 27 mm) (Table 3).The resistance of Gram-negative bacteria may be due to the presence of lipopolysaccharides in their cell wall, thus preventing the possible active components of date extracts to crossing and lysing their cytoplasmic membranes [25, 37].

Table 3

Antibacterial activity of methanolic dates extracts compared to antibiotics

Varieties	IZD* (mm)		Antibiotics	IZD* (mm)	
	E. coli	***S. aureus***		***E. coli***	***S. aureus***
Ghars	18.7±0.6^{d}	26.3±1.5^{cd}	Cefazolin	24.6±1.1^{b}	32.6±0.7^{a}
Tamesrit	26.3±1.5^{ab}	43.0±1.0^{a}	Colistin sulfate	13.0±1.7^{e}	16.0±2.1^{d}
AdemFgig	24.7±1.2^{b}	24.3±2.1^{d}	Tetracycline	10.0±1.4^{f}	26.0±1.2^{c}
Akerbouch	27.0±1.0^{a}	35.3±3.1^{b}	Ampicillin	21.0±0.6^{c}	25.0±1.0^{c}
BentKbala	25.3±0.6^{ab}	29.3±0.15^{c}	Fosfomycin	35.0±1.5^{a}	29.0±2.5^{b}
Bouzror	22.0±1.0^{c}	27.0±1.0^{cd}	Ceftazidime	6.0±0.1^{g}	6.0±0.0^{f}
H'mira	11.0±1.0^{e}	15.0±0.1^{e}	Chloramphenicol	20.3±0.4^{d}	7.6±0.0^{e}

* Mean values ± SD, n=3 ($p<0.05$), IZD: Inhibition Zone Diameter. The Means followed by the letters a, b, c, d, e, f and g in the same column are significantly different ($p<0.05$)

The methanolic extract of *Tamesrit* variety which was significantly ($p<0.05$) the most effective, showed the maximum IZD against *S. aureus* (43 mm: nearly 50% of the population were inhibited) and *E. coli* (26.3 mm: nearly 30% of the population were inhibited) (Table 4).

Table 4

Minimum inhibitory concentration (MIC) and percentages of growth inhibition of methanolic dates extracts

Varieties	***E. coli***						
	Concentration of extract (g/mL)					MIC (g/mL)	I%
	0.20	0.16	0.12	0.08	0.04		
Ghars	-	-	-	-	+	0.08	20.8
Tamesrit	-	-	-	-	+	0.08	29.2
AdemFgig	-	-	-	-	+	0.08	27.4
Akerbouch	-	-	-	-	+	0.08	30.0
BentKbala	-	-	-	-	+	0.08	28.1
Bouzror	-	-	-	-	+	0.08	24.4
H'mira	-	-	-	+	+	0.12	12.2
Varieties	***S. aureus***						
	Concentration of extract (g/mL)					MIC (g/mL)	I%
	0.20	0.16	0.12	0.08	0.04		
Ghars	-	-	-	-	+	0.08	29.2
Tamesrit	-	-	-	-	-	<0.04	47.8
AdemFgig	-	-	-	-	+	0.08	27.0
Akerbouch	-	-	-	-	-	<0.04	39.2
BentKbala	-	-	-	-	-	<0.04	32.6
Bouzror	-	-	-	-	+	0.08	30.0
H'mira	-	-	-	-	+	0.08	16.7

+: presence of growth, -: no growth, I%: The percentage of growth inhibition

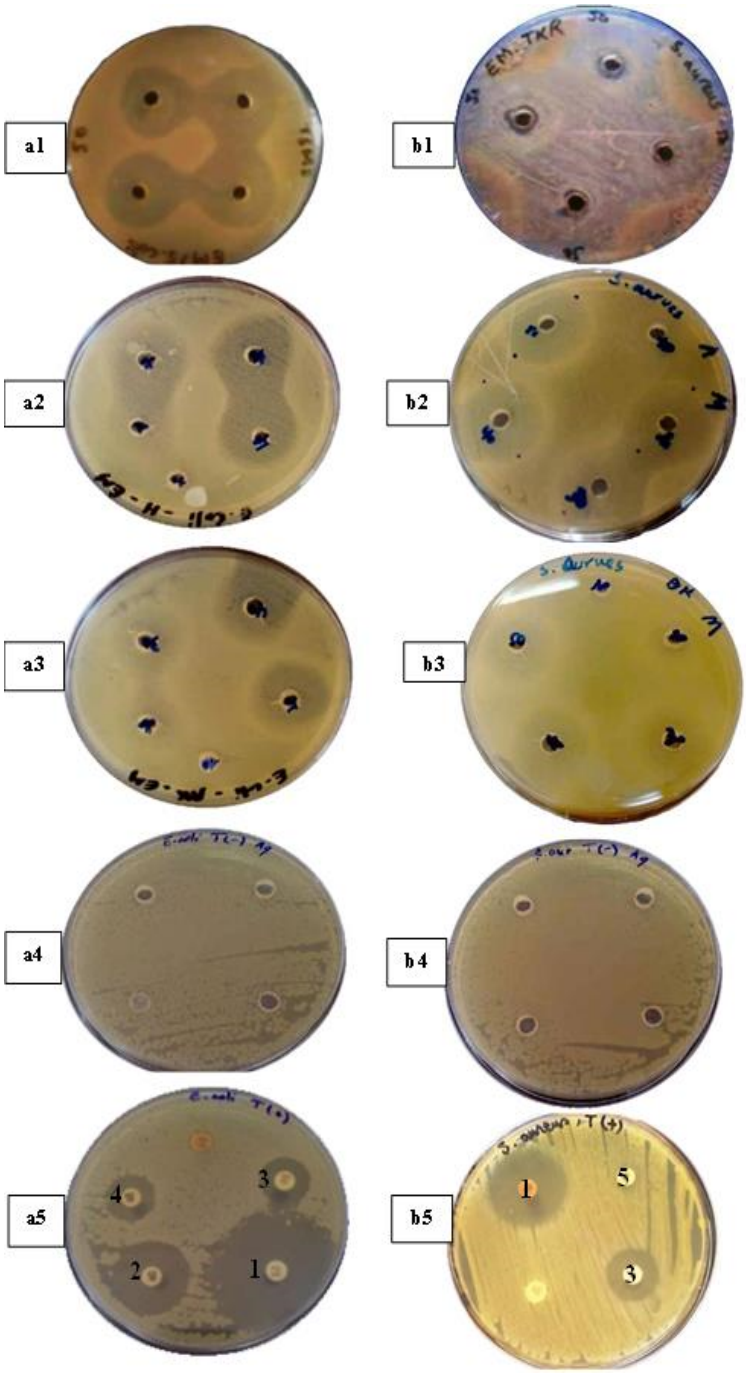

Figure 1. Antibacterial activities of methanolic extracts of some date's varieties compared with negative (a4, b4) and positive (a5, b5) controls against *E. coli* (a) and *S. aureus* (b) strains

Designation in Figure 1

Antibiotics for positive control: 1: Fosfomycin, **2:** Cefazolin, **3:** Colistin sulfate, **4:** Tetracyclin, **5:** Chloramphenicol

a1, a2 and a3: effect of *Tamesrit, Akerbouch* and *Bent Kbala* respectively against *E. coli*

b1, b2 and b3: effect of *Tamesrit, Akerbouch* and *Bent Kbala* respectively against *S. aureus*

Minimum inhibitory concentration (MIC) values below 0.04 g/mL are noted for *Tamesrit, Akerbouch* and *Bent Kbala* extracts against*S. aureus* (Table 4). Whereas for both strains, a MIC of 0.08g/mL is recorded for the methanolic extracts of majority of dates cultivars excepting *H'mira* extract which showed a MIC of 0.12g/mL (I% = 12.2%) to inhibit the growth of *E. coli*.

Extracts of *Akerbouch* and *Bent Kbala* varieties gave an interesting IZD for Gram positive bacteria of 35.3 to 29.3 respectively mm and for Gram negative bacteria of 27 to 25.3 mm respectively (Table 3, Figure 1). A study conducted on the bacterial activity of three Algerian varieties *Ghars, Deglet Nour* and *Mech Degla* on some bacterial species gave IZDs of 7.5 to 9.5 mm against *E. coli* which are clearly lowers to the diameters we obtained with all methanolic extracts on the same germ [38].However a study of the antibacterial activity of methanolic extracts of Saudi dates gave IZDs of 16 ± 0.20 mm on *S. aureus* and 11 ± 0.00 mm on *E. coli*[35];these values correspond to the minimum IZDs found for our varieties. In another study, the antibacterial activity of methanolic Nigerian dates extracts gave IZDs of 12 to 18 mm against *E. coli* [39]; values comparable to those obtained with *H'mira* and *Ghars* cultivars extracts in the present study which exhibit the lowest antibacterial activity.

On the other hand, for the control antibiotics used, Fosfomycin and Cefazolin gave a maximum inhibition diameter of 32.6 mm and 35 mm against *S. aureus* and *E. coli* respectively. The interest of the results we obtained is that all the antibiotics showed an antibacterial activity comparable to that of dates extracts or even less than some (Table 3). Effectively, the methanolic extract of *Tamesrit* variety (IZD=43 mm) was more active (P<0.05) than all antibiotics against *S. aureus* (IZD maximum of 32.6 mm for cefazolin). The results of this study showed that *S. aureus* were highly resistant to Chloramphenicol and ceftazidime while *E. coli* resisted to ceftazidime and tetracycline versus the active methanolic extracts of the different date cultivars. The presence of flavonoids, saponins, terpenoids and tannins, may be involved in the bioactivity of plant extracts, these chemical groups have been demonstrated in other studies conducted on the evaluation of antibacterial activity [29].The studied dates extracts (Table 1) contain heterogeneity of chemical compounds that could explain the antibacterial activity observed.

Conclusion

The sensitivity of the studied bacteria (*S. aureus* and *E. coli*) was more apparent for the extracts of *Tamesrit* variety followed by those of *Akerbouch* and *Bent Kbala,* this result is very important because it provides an answer element for the choice of some dates varieties for a possible therapeutic use. The date could be used as a bioconservative in the food industry which gives added value to this fruit playing both a role of preservative and stabilizer during food storage by their antibacterial effects but also able to improve their organoleptic and nutritional qualities by its contribution in interesting elements such as the polyphenolic compounds and the antioxidant power, so it would be a very interesting functional food ingredient. The difference between the antibacterial activity of the two date extracts (aqueous

and methanolic) is difficult to explain because both extracts contained all sought metabolites, but not in the same proportions. So, identification and quantification of active components is necessary and could shed more light on the difference in the biological activities of dates extracts.

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Antioxidant properties and color characteristics of sponge cakes containing functional components

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Abstract

Introduction. This study had investigated the effects of the addition of functional components (Jerusalem artichoke, cocoa husks and einkorn) on the color, antioxidants, and functional properties of sponge cakes.

Materials and methods. The antioxidant activities of sponge cakes were evaluated by methods: ABTS, CUPRAC, FRAP and DPPH assay. Sample analysis also included measurement of color properties in CIEL*a*b* color system using colorimeter.

Results and discussion. The smallest antioxidant activity was observed in 100% wheat flour cake (control) evaluated by four methods, as DPPH no detected. The antioxidant activity on cocoa husks powder and cake prepare with cocoa husks has been reported on the four methods for different mechanisms of antioxidant action. The antioxidant activity of functional components - cocoa husks powder and einkorn wholemeal flour, is the highest determined by CUPRAC-assay (203,75 ± 0,55 mM TE/g DM; 117,94 ± 0,24 mM TE/g DM) and ABTS-assay (107,55 ± 0,68 mM TE/g DM; 520,85 ± 5,71 mM TE/g DM), respectively. The sponge cake with 50% einkorn wholemeal flour could be developed as a functional food with more effective antioxidant properties. The lightness (58.50±7.43), a* (9.90±1.93) and b* (26.31±0.85) values for crust control were not significantly different from those of the cake with einkorn wholemeal flour (L* = 60.48±6.27; a* = 9.42±1.69; b* = 25.68±1.44), so carotenoids and lutein was considered to give a good approximation to the color that einkorn wholemeal flour communicates to cakes. The crumb color on the control sample was similar to that of the cake with einkorn wholemeal flour. According to these results, cakes with Jerusalem artichoke (ΔE = 6.62) and cocoa husks where (ΔE = 23.53) the total color difference was appreciable by the human eye.

Conclusions. The sponge cake with einkorn wholemeal flour is with more effective antioxidant properties. The color on the control was similar to that of the cake with einkorn wholemeal flour.

Introduction

The quality of cake depends on the quantity and quality of ingredients especially the flour used in preparation. It was found that mixing two or more of different materials will help to solve the deficiency problem of cereal as low nutritional value. Special attention has given to the use of natural antioxidant because of the world wide trend to avoid or minimize synthetic food additives [1]. Flour contributes a major portion of cake and replacement of refined flour with nutrient-rich flour enhances nutritional profile but makes product development tricky. The production of cake from wheat, soybeans, cassava flour, maize flour and lupin flour has been reported [2, 3] .

Research studies and consumer demands show that natural products can be used to improve the textural and functional properties of cakes. Studies [4] reported that the use of barley flour in cakes affects nutritional and functional properties. Apple pomace incorporated into wheat flour led to higher acceptable quality of the cakes with 14.2% fibre content when 25% flour was replaced with apple pomace [5]. Green tea powder substituting some flour in sponge cakes pro duced a green tea cake with more effective antioxidant properties, as well as higher content of dietary fibre [6]. In other studies [7] banana powder was replaced with flour. According to the results, sponge and layer cakes with the inclusion of ripe banana generally led to a decline in the specific volume and hardness compared to the control. Changes found in the colour of the crumb and crust are similar for sponge and layer cakes, with darker crumbs and crusts as ripe banana flour is incorporated. These changes should be explained by the darker colour of banana flour resulted from the browning, suffered during the drying process of these flours. By the replacement of wheat flour with gamma aminobutyric acid, the bioactive characteristics of cakes were increased and this was found to be beneficial to human health [8]. Some studies have disclosed the potential sources of natural antioxidants on the bakery products. For example, the rye bread showed better antioxidant properties and higher antioxidant contents when compared to wheat roll [6, 9].

The addition of different flours to bakery products creates an opportunity to combine beneficial technological properties with beneficial biological health promoting properties.

Literature review

Sponge cake is a type of sweet bakery product characterized by its aerated and soft crumb and by its thin coloured crust. This product is produced all over the world and is decorated with different fillings, colours and flavours to create different kinds of cakes. In general, it is associated with celebrations and meetings, and it must fit to high-quality standards required by the consumers [10].

As health promoting substances, phytochemical and nonnutritive substances can be considered functional in foods [11, 12].

The cacao husks are considered as a valued source of dietary fibers, mineral elements on the basis of potassium, magnesium, calcium, proteins with balanced amino acidic composition, and polyphenolic compounds which manifest a strong antioxidant activity [13-15]. Consumption of dietary fibers offers health benefits including protection against cardiovascular diseases, cancer, reduction blood serum cholesterol and regulation of blood glucose levels [16]. Cocoa pod husk are used traditionally as medicine to treat the pains of pregnancy, fever and coughs [17]. It is proved [13] that in cacao beans husks the quantity of dietary fibre varies from 38 % to 44 %, as the mean insoluble fibre concentration is 64.5% of total fibre quantity. A study [18] was made of the texture, composition, appearance, colour

and descriptive sensory analysis of low-fat chocolate muffins in which part of the oil ingredient (25%, 50% and 75%) had been replaced by soluble cocoa fibre and full-fat (no fat replacement) control sample to which cocoa powder had been added for comparison purposes. The results indicate that soluble cocoa fibre is an encouraging option for replacing oil in a chocolate muffin formulation. The main advantages were that adding soluble cocoa fibre gave muffins higher moisture and a more tender and crumbly texture, as they were more fragile than the control, and reduced the signs of hardening during storage.

Jerusalem artichoke powder made from Jerusalem artichoke (*Helianthus tuberosus* L.) roots is a valuable product, rich in inulin, as well as vitamins and minerals. According patent by Zhelenkov [1999] has developed and published new technologies for the preparation of confectionary, baker's and pastry products with which the biologically active substances in topinambur flour defining its curative, preventive and dietetic properties are kept. He has recommended the inserting of topinambur flour in confectionaries and pastry food products to be in optimum quantity from 1 to 10 % of the total mass of the components according the recipe. Products of fructans-containing plants such as Jerusalem artichoke become increasingly interesting for application in food as they do not contain bitter taste compounds and therefore constitute a palatable functional ingredient, which may be applied as substitute of cereal flour in bakery products. Koryachkina et al. [19] have regarded the possibilities for the use of topinambur flour in the production of pastry food goods intended to ill people with sugar diabetes type 2. In the same aspect Sinyakovskaya et al. [20] suggest compositions and technologies of sugar-free and sweetened biscuits containing flour of topinambur tubers. The have found that the inserting of topinambur flour in sweetened and sucrose-free biscuits (with sorbitol or fructose) in amount up to 7 and up to 5 % of white wheat flour mass, respectively, has not worsened the structural and mechanical properties of the sponge cakes and biscuits. The topinambur flours brings to both kinds of biscuits a sweet taste, specific odor, brown color with gray nuance, and on the other hand decreases their energetic value and increases their biological activity.

Fibers, and more particularly the soluble ones, like inulin and fructooligosaccharides (FOS), are known to provide health benefits like stimulation of beneficial colonic bacteria (prebiotic capacity), reduction in bowel transit time, increase mineral absorption, improve immune response, and prevent diseases like intestinal infections, colorectal cancers, obesity, cardiovascular diseases and type II diabetes[21, 22].

Einkorn (*Triticum monococcum* L.) is a diploid hulled wheat appreciated for its excellent nutritional properties, including high protein, carotenoids, β-glucans and antioxidants contents [23-25], and as such it is a promising candidate for the development of functional bakery products. Einkorn-enriched cookies had higher ash, polyphenols, carotenoids, antioxidants and beta-glucans content than pure wheat flour cookies, and might possibly be classified as functional foods [25]. Einkorn wheat flour is suitable for the development of lutein-rich functional foods because lutein amounts to 8.41μg.g–1 d.m. on average [24]. Such food products are extremely healthful in old age because ageing patients suffer from macular degeneration which may result in blindness [23].

Current studies into free radicals have confirmed that foods rich in antioxidants play an essential role in the prevention of cardiovascular diseases and cancers and neurodegenerative diseases, as well as inflammation and problems caused by cell and cutaneous aging [26, 27].

Since some of synthetic antioxidants had toxigenic, mutagenic, and carcinogenic effects and some natural antioxidants were effective in enhancing the shelf life of bakery products but less effective than synthetic antioxidants, there is a great demand for the use of new natural antioxidants in food, especially in bakery products [6, 28, 29].

Color is one of the major attributes which affects the consumer perception of quality, holds a preeminent position in food acceptance [30]. At the point of purchase the consumer uses appearance factors to provide an indication of freshness and flavor quality. Consumers have a preferred color for a specific item [31].

The application of colorimetry offers an objective way of color assessment because it is based on the whole visible spectrum and makes it possible to obtain the real chromatic profile of food products. The objective measurement of color is of great importance for food producers due to the relationship existing between color and the acceptability [32].

Change of biscuits color during baking was a dynamic process in which transitory colors occurred as result of baking. The biscuits from 100% barley flour, a very visible change of color has been noticed even after 5 min. of baking ($\Delta E > 6$). From stored biscuits, the biggest change of color has been noticed with biscuits from 100% wheat flour after 6 ($\Delta E = 16.49$) and 12 months ($\Delta E = 14.29$) of storage. Browning development in biscuits begins when sufficient amount of drying has occurred. Moreover it was associated with the recipe (reducing sugars, leavening agents, salt, amino acids, etc.) and baking conditions (temperature and time). Browning was the final step of both the Maillard reaction and caramelization, one of the end-points of the baking process and the final result of sugar degradation during baking [33].

The above-presented brief review on available data clearly identifies the lack of sufficient scientific evidence about the effects of these functional components on cakes antioxidant properties and color characteristics.

The aim of this work was to evaluate color and antioxidant properties of sponge cakes enriched with functional components (Jerusalem artichoke powder, cocoa husk powder and einkorn wholemeal flour) and its utilization partially, substituted of wheat flour at levels of 20%, 35%, 50% as a natural source of antioxidants in cake making.

Materials and methods

Materials and sponge cakes preparation

Raw materials such as wheat flour of type 500 – ash content 0.5% (GoodMills, Bulgaria EAD), granulated sugar (Zaharni zavodi AD), eggs (local market) used in the current study. A control cake was prepared, following a traditional technology and formulation [34]. The batter formulation of the control cake was as follows (based on flour weight): egg yolk 43.23%, egg white 96.77%, refined granulated sugar 83.87%, and wheat flour 100%. In particular, a double mixing procedure was applied by partitioning whipping of whites and egg yolks. Jerusalem artichoke powder (JAP), cocoa husk powder (CHP) and einkorn wholemeal flour (EWF) were added into sponge cake flour at different levels 20, 35 and 50%, by replacing wheat flour, respectively. Each sponge cakes batter of 95 g was poured out in metallic forms and baked in an electric oven at 180°C for 30 min.

Evaluation of antioxidant activities of flours and sponge cakes

DPPH radical scavenging activity. The ability of the extracts to donate an electron and scavenge DPPH radical was determined by the slightly modified method of Brand-Williams et al. [35]. Freshly prepared 4×10^{-4} mol methanol solution of DPPH was mixed with the samples in a ratio of 2:0.5 (v/v). The light absorption was measured at 517 nm. The DPPH radical scavenging activity was presented as a function of the concentration of Trolox® -

Trolox® equivalent antioxidant capacity (TEAC) and it was defined as the concentration of Trolox® having equivalent AOA expressed as μmol TE/g dw.

ABTS radical scavenging assay. The radicals scavenging activity of the investigated extracts against radical cation (ABTS•+) was estimated according to the previously reported procedure with slight modifications [36]. The results were expressed as TEAC value (μmol TE/g dw).

Ferric-reducing antioxidant power assay (FRAP*).* The FRAP assay was carried out according to the procedure of Benzie and Strain (1996) [37]. FRAP assay measures the change in absorbance at 593 nm owing to the formation of a blue colored Fe (II)-tripyridyltriazine compound from colorless oxidized Fe (III) form by the action of electron donating antioxidants. The results were expressed as μmol TE/g dw.

Cupric ion reducing antioxidant capacity assay (CUPRAC). To a test tube, the solutions were added as follow: 1 mL of CuCl2 solution (1.0×10^{-2} M), 1 mL of neocuproine methanol solution (7.5×10^{-3} mol), and 1 mL NH4Ac buffer solution (pH 7.0), and mixed; 0.1 mL of sample followed by 1 mL of water was added (total volume = 4.1 mL), and mixed well. Absorbance against a reagent blank was measured at 450 nm after 30 min [38]. Trolox was used as standard and total antioxidant capacity of herbal extracts was measured as μmol TE/g dw.

Measurement of color of sponge cakes

The instrumental measurement of the cakes color was carried out with a colorimeter Color-guide 45/0 Colorimeter, BYK-Gardner Inc, USA, and the results were expressed in accordance with the CIELAB system. Color was measured at four predetermined places of the sponge cakes crust and crumb. The parameters determined were L* (L* = 0 [black] and L* = 100 [white]), a* (–a* = greenness and +a* = redness), b* (–b* = blueness and +b* = yellowness). The dominant wavelength (DW) of a color = a*/ b* (color tone).

$$DW = a^*/ b^*$$

Colorimeters give measurements that can be correlated with human eye-brain perception, and give tristimulus (L*, a* and b*) values directly. Determined is correlation between color parameters and visual sensory evaluation of color (TC) [39, 40].

Chroma, C*, is the aspect of color in by which a sample appears to difference from a gray of the same lightness or brightness, as defined by the following equations:

$$C^* = \sqrt{a^{*2} + b^{*2}}$$

The total color difference (ΔE*) between the control cake and the sponge cakes with functional ingredients was calculated as follows:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2},$$

as: $\Delta L^* = L_1 - L_0$; $\Delta a^* = a_1 - a_0$; $\Delta b^* = b_1 - b_0$.

The values used to determine if the total color difference was visually obvious were the following.

$\Delta E^* < 1$ color differences are not obvious for the human eye;

$1 < \Delta E^* < 3$ color differences are not appreciative by the human eye;

$\Delta E^* > 3$ color differences are obvious for the human eye [39, 41].

Results and discussion

Evaluation of antioxidant activities of flours and sponge cakes

The results from antioxidant activities of sponge cakes were presented (Figure 1) evaluated by four methods, based on different mechanism (DPPH, ABTS, FRAP and CuPRAC). The antioxidant activity in the einkorn wholemeal flour saved when the batters were baked.

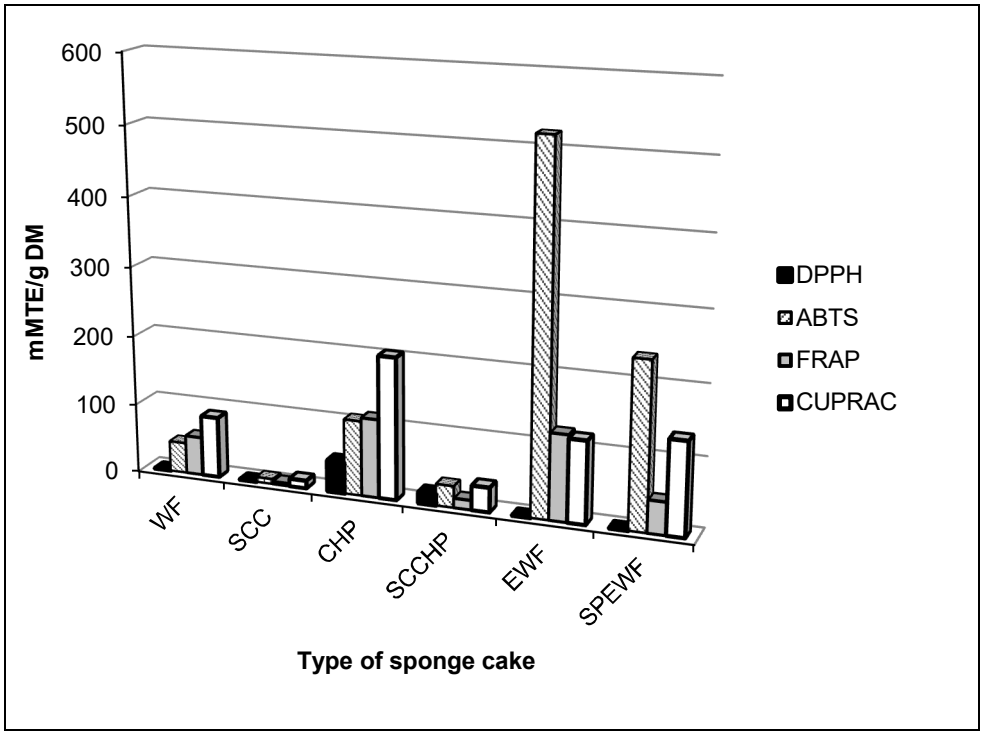

Figure 1. Antioxidant activity (mMTE/g DM) in flours and sponge cakes:
WF – wheat flour;
SCC – sponge cake control;
CHP – cocoa husks powder;
SCCHP – sponge cake with 35% cocoa husks powder;
EWF – einkorn wholemeal flour; SCEWF – sponge cake with 50% einkorn wholemeal flour.
** mM Trolox Equivalents/g dry matter

The smallest antioxidant activity was observed in 100% wheat flour cake (control) evaluated by four methods, as DPPH no detected.

The total antioxidant capacity determined by the free radical scavenging activity (DPPH-assay) of cocoa husks powder and sponge cake with 35% cocoa husks powder is 45.03 and 15.89 mM TE/g DM. The antioxidant properties for cakes with functional components determined by ferric reducing antioxidant power (FRAP-assay) for cake with 35% cocoa

husks powder – 30.88 mM TE/g DM and the cake with 50% einkorn wholemeal flour is 237.53 ± 7.08 mM TE/g DM. The antioxidant activity of functional components - cocoa husks powder and einkorn wholemeal flour, is the highest determined by CUPRAC-assay (203.75 mM TE/g DM) and ABTS-assay (520.85 mM TE/g DM), respectively.

The cakes with 35% cocoa husks powder and control have highest the antioxidant activity on CUPRAC, as sponge cake with 50 % einkorn wholemeal flour the highest scores are evaluated in relation to the free radical ABTS. Of the two methods of electron transfer (FRAP и CUPRAC), CUPRAC shows a higher antioxidant capacity compared to the samples tested. The antioxidant activity on cocoa husks powder and cake prepare with cocoa husks has been reported on the four methods for different mechanisms of antioxidant action.

A significantly higher content in conjugated phenols and total carotenoids was reported in water cookies with *T. monococcum* [42, 43], and was attributed to the superior concentration in einkorn kernels and flour of these compounds.

The sponge cake with 50% einkorn wholemeal flour could be developed as a functional food with more effective antioxidant properties.

Color of sponge cakes

Measurements of color properties for the tested compositions of sponge cakes with different functional components were conducted on crust and crumb of fresh cakes.

Crust color of cakes. The lightest samples (highest L* values) were those in which 50% of the flour had been replaced by einkorn wholemeal flour; the lightness values fell significantly as add 20 % Jerusalem artichoke powder (49.60±6.73). The sponge cake with 35 % cocoa husks powder had lowest values of a* and b* indicating a significantly brighter and more saturated brown-orange colour (Table 1).

Table 1

Crust color values of sponge cakes

Color characteristics[1]	Type of sponge cake			
	Control	With JAP	With CHP	With EWF
L*	58.50±7.43	49.60±6.73	54.16±2.48	60.48±6.27
a*	9.90±1.93	10.45±1.10	7.63±0.87	9.42±1.69
b*	26.31±0.85	23.99±1.47	20.13±1.37	25.68±1.44
DW	0.38	0.44	0.38	0.37
C*	28.11	26.17	21.53	27.35
ΔE	-	9.21	7.88	2.14
TC	0.86	1.23	1.22	0.83

[1] The values are average ± SD ($p \leq 0.05$).

The samples with 50% einkorn wholemeal flour and control have the highest values of b* (yellow component) indicating a significantly brighter and more saturated yellow color. The lightness, a* and b* values for control were not significantly different from those of the cake with einkorn wholemeal flour, so carotenoids and lutein was considered to give a good approximation to the color that einkorn wholemeal flour communicates to cakes. The same products had the highest value of chroma of crust. The lowest values for chroma were detected at the crust for the cake containing cocoa husks as fiber source. The dominant

wavelength (DW) of a color at crust have the highest values on cake containing Jerusalem artichoke powder. According to these results, cakes with Jerusalem artichoke and cocoa husks where the ΔE* was appreciable by the human eye (ΔE*> 3). According Martínez-Cervera *et al*. [18] adding soluble cocoa fibre gave a fair change of color in muffins.. However, there are points that require improvement, such as the loss of height, perception of bitter taste and a certain surface stickiness.

The correlation between color parameters on crust and visual sensory evaluation of color (TC) on the control sample was similar to that of the cake with einkorn wholemeal flour.

Crumb color of cakes. The variations in the crumb color of the cakes with functional components as flour replacer were similar to the variations in crust color (Table 2). The cake with einkorn wholemeal flour was the lightest and the b* values showed that this sample had a brighter color. The crumb color on the control sample was similar to that of the cake with einkorn wholemeal flour. The color tone of crumb have the highest values on cake containing cocoa husks. The lowest values for chroma were detected at the crumb for the cake containing Jerusalem artichoke powder as fructooligosaccharide source. This would be in agreement with the ΔE* values, where only the einkorn wholemeal replacement formulation showed a color difference that was not appreciable by the human eye (ΔE*< 3). Gedrovica & Karklina [44] studied characteristics of cakes enriched with Jerusalem artichoke powder /flour of topinambur tubers/ at a concentration of 10, 20, 30, 40, 50%. The cakes enriched with Jerusalem artichoke powder (at a concentration of 30 and 40%) stayed soft longer during the storage time (two days) than control samples without this powder. The highest content of moisture was observed in cakes enriched with Jerusalem artichoke powder at a concentration of 20 and 30%. The concentration of Jerusalem artichoke powder and moisture with a probability of 95% substantially influenced the color components L*a*b*. The highest changes in color were reflected by the values L* (darkness) a* (redness). The best quality of cakes was determined in samples with a 30% addition of Jerusalem artichoke powder. Determined is correlation between color parameters and visual sensory evaluation of color (TC), as the highest values for crumb cake have product with cocoa husks.

Table 2

Crumb color values of sponge cakes

Color characteristics[1]	Type of sponge cake			
	Control	With JAP	With CHP	With EWF
L*	59.41±5.34	52.84±1.07	36.27±4.11	60.88±2.69
a*	0.96±0.86	1.35±0.32	5.16±0.56	1.47±0.47
b*	13.11±1.64	12.36±1.39	13.79±2.74	15.17±1.24
DW	0.07	0.11	0.37	0.10
C*	13.15	12.43	14.72	15.24
ΔE	-	6.62	23.53	2.58
TC	2.46	4.11	19.32	3.17

[1] The values are average ± SD ($p \leq 0.05$).

Conclusion

Sponge cakes with functional components had higher levels of antioxidants and antioxidant activity when compared with their respective controls. The antioxidant activity in the einkorn wholemeal flour saved when the batters were baked. Results of instrumental measurements of color of crust and crumbe of sponge cakes, obtained with the colorimetry (in CIE and CIE L*a*b* systems) are in good agreement with sensory evaluations of color and brightness of cake samples. The lightness, a* and b* values for crust control were not significantly different from those of the cake with einkorn wholemeal flour, so carotenoids and lutein was considered to give a good approximation to the color that einkorn wholemeal flour communicates to cakes. The crumb color on the control sample was similar to that of the cake with einkorn wholemeal flour. According to these results, cakes with Jerusalem artichoke and cocoa husks where the ΔE* was appreciable by the human eye. As a result of the good functionality of used functional components in cake formulation, were very good ingredient in composite flours.

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Impact of cryoprotection on minimization of ascorbic acid losses in freezing of berries

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Abstract

Introduction. Minimization of ascorbic acid losses during freezing and frozen storage of berries can be achieved by various methods of cryoprotection. The objectives of this research are to confirm the impact of different cryoprotectors on minimization of ascorbic acid losses during freezing and frozen storage of berries.

Materials and methods. Bilberries, blackberries, and chokeberries in fresh, frozen and defrosted states were researched in this article. The 10-percent solutions of mono and disaccharides, the 1-percent solutions of organic acids and the 15-percent solution of inorganic salt (magnesium chloride) were chosen as cryoprotectors. The amount of ascorbic acid in defrosted berries, which was defined by the well-known method (with sodium 2.6-dichlorphenolindofenolate), was the criterion to confirm the effectiveness of cryoprotectors.

Results and discussion. The traditional methods to freeze the berries had proved the well-known fact of the significant losses of ascorbic acid. The latter made up 16.8 to 26.3 percents in frozen products and 55.6 to 71.0 percents in those defrosted. This was the result of cryogenous damages of berries' cells by ice crystals, and thereinafter the cause of ascorbic acid oxidation by oxidoreductases and its leakage together with cellular juice during berries' defrosting.

The berries processed with cryprotective solutions before freezing were believed to keep the holity of their structure during freezing, long-term (for 12 months) frozen storage, and defrosting. Therefore, the effect of ascorbic acid retention in most cases exceeded 80 percents, relatively to its amount in fresh raw materials. Thanks to protective action of cryoprotectors at the stage of berries freezing, the ascorbic acid losses did not overcome 16.8 to 26.3 percents; after frozen storage for 12 months and defrosting, the residual amount of ascorbic acid made up 62.8 to 83.5 percents. Meanwhile, the control samples (berries frozen without protectors) had got ascorbic acid left on the level of 22.4 to 33.6 percents.

The authors of this article proposed to classify the cryoprotectors by four categories according to their cryoprotective effect (relatively to ascorbic acid); the cryoprotectors which showed the effect of ascorbic acid retention less than 40 percents were not recommended to further usage. The compound cryoprotectors turned to be more effective than those simplex. Only the berries frozen by the improved method (with cryoprotectors) had received the highest grade (5 out of 5) by all of the indices.

Conclusions. Realization of theoretical knowledge in studying the cryoprotectors by cryobiology scientists had shown the positive effect of cryoprotection in berries freezing.

Introduction

According to the prognoses by analytics, the demand for frozen fruit-and-berry and vegetable products is growing constantly in the entire world, and the amount of their consumption is increasing on almost 4 percents [1, 2]. It is the regulation proved.

The usage of artificial cold causes minimal changes in nutritional and biological value of the raw materials and foodstuffs obtained from them, in their quality and sensory indices [3]. Along with that, the method to preserve the food materials by freezing, regarding its economy and specific energy supply, has got some significant advantages in comparison with methods of thermal preservation (pasteurization, sterilization, drying etc.) [4].

This is no wonder that the specialists in food science give priority to the method of cold preservation of raw materials and final foodstuffs, in all of its modifications and variants of the usage [5, 6, 7].

Meanwhile, in Central and East Europe the domestic frozen plant products are not yet issued in reasonable amounts [8], especially fruit and berries; those sold at the markets are mostly of low quality due to disadvantages in the traditional methods of freezing and frozen storage of half products [9]. Biological objects are often exposed to significant cryogenous damages during freezing [8, 9]; consequently, cellular juice and all the biologically active substances that it contains (vitamins, mineral elements, minor components as the valuable constituents of fruit-and-berry raw material) get lost in defrosting [10].

Henceforth, the improvement of the existent low-temperature technologies of fruit, berry, and vegetable raw procession (particularly, due to the combination of the impact of cold with other physical and technological factors) is relevant for the producers of frozen half products [11, 12, 13].

The analysis of up-to-date scientific works on the topic of our research evidences that the mechanisms of cryogenous damages of plant cells and the methods to protect the latter are studied profoundly in cryobiology [14, 15] which is comparatively young branch of general biology. Our studies of fundamental and applied researches accomplished in the 1950s-1970s at the cryobiological centers of USA, Great Britain, France, Japan etc. allowed generalizing the results of the first endeavors in cryobiology. They were further developed in the works by R.A. Carrow [16] who studied the behavior of different parts of the live cell in freezing; A. Bilous and V. Gryshhenko [9] who researched the problems of cryogenous preservation of reproductive cells; Ye. Gordiyenko [17] who dedicated his works to the low-temperature preservation of cellular suspensions.

The general conclusion is the following: the development of destructive crystal making (both inside and outside the plant cells) can be crucially slowed down if the freezing of cells and tissues goes on with a help of various cryoprotectors which benefit the modification of liquid phase structure and the character of crystal making.

Because the natural biological objects in medical and agricultural raw materials are similar by chemical composition and cell structure, it is expedient to use the experience gained by aforesaid theorists in food technologies. The number of the works published is small enough [11, 18]; therefore, each new research in this trend will contribute to the development and usage of the novel effective methods of freezing whose main destination is the retention of the maximal amounts of biologically active substances (ascorbic acid, first of all, as the most liable component) from raw materials in the final product.

The objectives of this research is to study the cryoprotective abilities of various compounds of both organic and mineral origin from the viewpoint of minimization of ascorbic acid losses during freezing, frozen storage, and defrosting of berries.

Materials and methods

Plant raw materials

We conducted the researches with bilberries, blackberries and chokeberries. After selection, washing, and contaminant removal, all of the researched specimens were processed with cryoprotective solutions of both organic and mineral origin, which were thoroughly described in the works on cryobiology [9, 14, 17] and thenceforth proved in our studies.

Cryoprotective solutions

Among over 20 different cryoprotective compounds, we chose mono and disaccharides (glucose, fructose, and sucrose), organic acids (citric, sorbic, and benzoic), and magnesium chloride for our research. The preliminary studies had shown the expedience to use of cryoprotective solutions with 10 and 15-percent concentration, and also the higher effectiveness of compound protectors [19]. Therefore, we grounded the compositions of cryoprotectors with the following proportions: sucrose (10 percents) and citric acid (1 percent); glucose (10 percents) and citric acid (1 percent); fructose (10 percents) and citric acid (1 percent); sorbic acid (1 percent) and benzoic acid (1 percent), and also simplex cryoprotectors – magnesium chloride (15 percents), sucrose (10 percents), glucose (10 percents), and fructose (10 percents).

Obtaining the frozen berries

After acceptation, washing, and contaminant removal, the berries were processed by cryoprotective solutions during 40–60 min at the room temperature. Then, they were frozen scattered in rapid freezer at the temperature of –35—37 °C, which corresponded to the parameters of rapid freezing [20]. The process lasted until the temperature –18 ± 1 °C in the middle of the berries scattered.

Frozen berries were packed into the packages of 500 grams, observing the requirements of package holity and hermetic sealing; stored during 12 months (the maximal term) at the temperature of –18 °C and relative humidity of no more than 95 percents. In preparing to freezing, the berries were defrosted at the temperature of 34–40 °C in the water bath. The berries frozen by the traditional technology, i.e. without cryoprotectors, served the control specimens.

Definition of vitamin C content

The content of vitamin C is the main biologically active component of the berries to determine their nutritional and biological value. That is why the level of its retention is the probable indicator to expose the perfection of the freezing technology. This index was defined in berries fresh, frozen and defrosted by the traditional technology (control), and frozen with a help of cryoprotectors. The method of vitamin C definition is well-known and based on the usage of sodium 2.6-dichlorphenolindofenolate [21].

Evaluation of sensory indices of fresh and frozen berries

Having based on the literary data and the results of our own researches, we widened the interpretations of the characteristics for sensory properties of fresh fruit, berries, and frozen half products made of them in order to give them the proper objectivity. That resulted in elaboration of five-point scale to evaluate every index, which would increase the requirements to the raw materials and guarantee the high quality of frozen products during the entire storage term and further defrosting [22]. The frozen products are supposed to

slightly differ from fresh raw by their sensory indices and qualitative composition (this should be the main criterion of perfection of the novel freezing technology). Thenceforth, we firstly presented the characteristics of both raw materials and the frozen half products obtained from them (Figure1).

Figure 1

Methods to evaluate the main sensory indices of fresh and frozen berries

Index	Research subjects	Characteristics
Appearance	fresh	clean, fresh, with stems (blackberries), without stems (bilberries and chokeberries), homogenous in maturity, with wax plaque, and with proper shape
	frozen	clean, frozen, with bluish plaque, turgid, not squashed, and with proper shape
Taste	fresh	immanent to the certain species, with the taste sour, sweet, astringent, slightly bitter, or spicy (or their combinations)
	frozen	immanent to the certain species, with the taste sour, sweet, astringent, slightly bitter, or spicy; the taste may slightly vary due to the chill stress
Color	fresh	immanent to the certain species, correspondent to harvest maturity; the color intensity is defined as the maturity marker
	frozen	immanent to the certain species; with no declinations from the natural color; the color intensity may increase due to anthocyanine synthesis as the reaction to the chill stress
Surface state	fresh	dry, clean, without illnesses, damages, and signs of withering; dependently on the pomological sort, may be moistened; with harvest maturity and the proper color; the peel is dense
	frozen	clean, slightly moistened, naturally turgid, without damages of the peel and cellular juice losses
Odor	fresh	proper to the certain species (light, strong, subtle, tender)
	frozen	proper to the certain species (light, strong, subtle, tender); may be gained as the result of the chill stress

Afterwards, the mentioned sensory characteristics of the berries were evaluated by the five-point scale elaborated by the authors of this article. The ‘5’ grade was given to the berries clean and fresh; of the intensive color; with clean surface, without defects and damages; with the intensive odor immanent to the certain species. The ‘4’ grade was given to the berries clean and fresh, without defects and damages (up to 5 percents of immature berries); with slightly perceptible strange smack and odor; of the color immanent to the certain species; with clean low-mat surface. The ‘3’ grade was given to the berries clean, fresh, without defects and damages (up to 7 percents of immature berries); with stable strange smack and odor; of low-intensive color.

The berries that have got the ‘1’and ‘2’ grades are not recommended for freezing. These are faded berries, not homogenous in shape, with defects (up to 10 percents of non-standard items); with unpleasant strange smack and odor, significant damages of the surface, the symptoms of negative biochemical processes (even rotting), and the natural color lost.

Results and discussion

Ascorbic acid in the berries fresh and frozen traditionally

The research got started from the evaluation of shifts of the ascorbic acid amount during freezing the berries by the traditional method, their frozen storage and defrosting. The results are presented in Figure 2.

Figure 2

Dynamics of shifts of the ascorbic acid amount in the berries frozen traditionally

Specimens to research	Ascorbic acid amount in the berries, mg per100 g			$HIP_{0,5}$
	Blackberries	Chokeberries	Bilberries	
Fresh berries	130.4	243.6	193.3	0.8
Frozen berries (control)	104.9	202.0	142.5	0.7
Frozen and defrosted berries (control)	48.5	108.1	56.1	0.9

The analysis of the figure data showed that the berries rapidly frozen by the traditional technology had already lost the certain amount of ascorbic acid. If to take its content in fresh berries for 100 percents, it got lowered on 19.6 percents in frozen blackberries, on 16.8 percents in chokeberries, and on 26.3 percents in bilberries. This was the result of destructive impact of extra and intracellular ice crystals on cellular membranes and subcellular structures. Consequently, the number of cells got destroyed, the cytoplasm membrane (or cellular carcass) got torn [23], and this all lead to the direct contacts between biologically active substances inside the cells and oxidoreductases. The latter enhanced the biochemical reactions of oxidation, leading to ascorbic acid decomposition.

Ascorbic acid losses got significantly increased during the berries' defrosting, due to the leakage of cellular juice from cryogenously damages cells, together with biologically active components dissolved in it. For example, this index has grown up to 62.8 percents in blackberries; 55.6 percents in chokeberries; 71.0 percents in bilberries. As a result, the nutritional and biological value of half products has sharply fallen, and thus the final products are believed to be hardly obtained from even the most qualitative raw materials.

The data from Figure 2 allowed concluding that the amount of vitamin C is different in various berries with similar conditions of freezing and defrosting. Undoubtedly, it is connected with qualitative and quantitative biocomponents' content, besides the factors mentioned above, and is the evidence of the direct correlation between the level of vitamin retention and the amount of sugars in the berries. This all can correspond with well-known theoretical data from cryobiology [9]: glucose, fructose, and sucrose are the natural cryoprotectors. For example, bilberries have the less content of sugars than blackberries and chokeberries, and therefore the level of ascorbic acid retention is lower. The berries' holity also depends on the structure and density of peel which makes them able to resist the cryogenous damages [24, 25].

Ascorbic acid in defrosted berries beforehand frozen with cryoprotectors

The comparison of the residual amount of ascorbic acid in the berries frozen with cryoprotectors and defrosted after the 12-month storage allowed us to answer several questions simultaneously. First of all, the question was how to evaluate the positive impact of cryoprotection on retention of the most precious and liable component (which is vitamin C) in defrosted half products. The second problem was the effectiveness of using either the complex or combined cryoprotector to freeze various biological objects. Finally, the third point was to prove the real possibility to choose the proper cryoprotector for different sort of raw fruit and berries to provide its maximal cryoprotection and thereto the minimal ascorbic acid losses.

Figure 3 represents the calculation of the amount of ascorbic acid (in percentage to the mentioned index in fresh berries): blackberries contain 130.4 mg / 100 g; chokeberries contain 243.6 mg / 100 g; bilberries 193.3 mg / 100 g. These indices are obtained in the berries frozen by the improved technology (with cryoprotectors) and defrosted after the 12-month storage.

Figure 3

Residual amount of ascorbic acid in defrosted berries

Cryoprotector	The residual amount of ascorbic acid, percents to its content in fresh berries		
	Blackberries	Chokeberries	Bilberries
$MgCl_2$ (15%)	76.8	70.7	62.4
Sucrose (10%)	78.7	76.5	64.0
Fructose (10%)	64.9	63.8	58.8
Glucose (10%)	75.8	64.2	57.7
Sucrose (10%) + citric acid (1%)	83.5	81.8	75.5
Fructose (10%) + citric acid (1%)	74.2	70.4	64.7
Glucose (10%) + citric acid (1%)	81.6	69.8	76.5
Sorbic acid (1%) + benzoic acid (1%)	62.8	60.5	58.4
Control (without cryoprotectors)	31.0	33.6	22.4

According to the data of the Figure 3, the positive influence of cryoprotectors was displayed in all of the objects: the level of ascorbic acid retention in the berries frozen by the improved technology and defrosted after 12-month storage exceeds the identical index for the berries frozen without cryoprotectors at all the stages of the experiment. Although the mechanisms of cryoprotective action are complicated and have not been yet discovered fully, it is possible to affirm that they would help minimize the results of minus temperatures' destructive impact during freezing and further defrosting of the berries. The data about the residual amount of ascorbic acid are good evidence of this fact.

In spite of the variety of cryoprotectors and their combinations chosen for the research, their influence on the objects studied has got its regulations. Having based on the theoretical data existing by now [See 26], we may say that the main point in activity of the cryoprotectors

is their ability to reduce the amount of water which can crystallize during freezing (and thereby to reduce the number of large ice crystals), to benefit the creation of small-crystal ice, and, subsequently, to protect the cell from the pernicious impact of minus temperatures.

The authors [7] supplemented this theory by the deductions about the cryoprotectors' ability to lower the freezing point of water (cryoscopic temperature); to gain the viscosity of solutions and therefore to retard the growth of ice crystals; to influence positively the processes of hydration of plant cells in defrosting.

Thenceforth, the authors of this article discovered that the positive impact of cryoprotectors usage in the technologies to freeze the raw berries (particularly, from the viewpoint of maximal retention of ascorbic acid) was the result of the combination of several aforesaid effects shown by researched cryoprotectors.

As for A. Belous and V. Gryshhenko, the leading specialists in cryobiology and cryomedicine [6], the cryoprotectors are to be chosen empirically, individually for each of the biological objects, because the universal principles to select the cryoprotector with the properties programmed for the certain object are not elaborated yet. According to Figure 4, the combined cryoprotectors are more effective than those simplex. The highest cryoprotective effect gets achieved in combination of sucrose (10-percent solution) and citric acid (1-percent solution): after 12-month frozen storage and further defrosting, blackberries and chokeberries retain over 80 percents of ascorbic acid, and bilberries retain 75.5 percents. Citric acid in the compound cryoprotectors serves as the polyfunctional substance to change the character of water crystallization in cells and intercellular space, and to support the stability of the structural-functional parameters in biological objects, as the authors [27] confirmed.

Generally, the vitamin value of the berries frozen with cryoprotectors is high enough; otherwise, this effect could not be reached with the traditional freezing technology. The data of Figure 4 eloquently show that the residual amount of ascorbic acid in the berries frozen without cryoprotectors oscillates from 22.4 to 33.6 percents of its content in the raw materials.

The similar regulation was noticed by other researchers. For example, Estonian scientists A. Noormets with co-authors (2006) indicated the influence of different conditions of freezing on the ascorbic acid amount in cowberries (Vaccinium sp.) [28]; C. Mullen with co-authors (2002) analyzed the antioxidant properties of frozen and defrosted red raspberries [29]. The positive influence of the preliminary procession of raspberries on the quality of final products during long-term frozen storage was also confirmed in the work [30]. We may also set up the analogy with the results reached by cryobiologists: the authors [31] confirmed the fact that the red blood cells frozen without cryoprotectors had been exposed to significant damages; particularly, 2 percents of them got destroyed completely. The implementation of cryoprotectors into the freezing environment could prevent such processes [14], and the usage of combined protectors could fully eliminate the damages of red blood cells in freezing / thawing cycles [32].

The rating scale to evaluate the cryoprotective effect of the substances researched

The data obtained by different scientists are the evidence the essential losses of ascorbic acid in raw fruit and vegetables frozen traditionally (without cryoportectors). The authors [33] showed that frozen wild strawberries had lost 60 percents of ascorbic acid, and the authors [34] observed that the percentage of ascorbic acid loss in vegetables had reached 65. These data are compatible with the results received by other Ukrainian specialists, including those from National University of Food Technologies. Actually, all of the results obtained

are the convincing argument on the favor of the usage of different cryoprotectors in the technologies of the plant raw freezing.

Therefore, the authors of this article elaborated the rating scale of the researched cryoprotectors to use it in practice. The protectors were classified into four categories by the level of ascorbic acid retention (this index was given the virtual name of 'the effect of cryoprotection'):

- First category – the effect of cryoprotection is 80 percents and higher;
- Second category – the effect of cryoprotection is 70–79 percents;
- Third category – the effect of cryoprotection is 60–69 percents;
- Fourth category – the effect of cryoprotection is 40–59 percents.

The substances with the effect of cryoprotection lower than 40 percents are not recommended to the usage as cryoprotectors.

The distribution of the protectors researched by the categories, according to the rating scale, is the following (Figure 4).

Figure 4
Distribution of the cryoprotectors researched by the effect of cryoprotection of the berries in freezing

Cryoprotector	Defrosted berries		
	Blackberries	**Chokeberries**	**Bilberries**
$MgCl_2$ (15%)	II	II	III
Sucrose (10%)	II	II	III
Fructose (10%)	III	III	IV
Glucose (10%)	II	III	IV
Sucrose (10%) + citric acid (1%)	I	I	II
Fructose (10%) + citric acid (1%)	II	II	III
Glucose (10%) + citric acid (1%)	I	II	II
Sorbic acid (1%) + benzoic acid (1%)	III	III	IV
Control (without cryoprotectors)	–	–	–

The data of Figures 3 and 4 are the evidence that the cryoprotective effect worked not only at the stage of freezing, but also during the long-term frozen storage and defrosting of half products. The combined cryoprotectors *sucrose + citric acid* and *glucose + citric acid* turned to be the most effective – their effect of cryoprotection exceeded 80 percents. The combined protector *fructose + citric acid* came third in effectiveness (the effect of cryoprotection was 64–74 percent). The same effect was shown by simplex protectors – *sucrose* and *magnesium chloride*.

There was an interesting fact that the same cryoprotector could show the different protective effect for different berries. For example, the compound protector *sucrose + citric acid* turned to belong to the 1st category by protecting blackberries and chokeberries, and to the 2nd category by protecting bilberries. The obtained results are attractive not only because of the actual positive cryoprotective effect shown, but also thanks to the possibility to find

the optimal cryoprotector for the certain kind of raw. Therefore, this would help significantly increase the vitamin value of frozen and defrosted half products obtained from any cultivated berries.

In general, we can foresee that the usage of all of the researched protectors would be effective for various fruit and berries. This is because the protectors' effect is on the average higher than 60 percents (by ascorbic acid amount), which is the good result for defrosted biological objects.

Sensory characteristics of frozen berries

The nomenclature of the indices to evaluate the quality of fruit, berries, and vegetables, regulated by the normative documents, includes mostly their sensory properties [35]. Thenceforth, we evaluated the organoleptic indices of bilberries frozen by both the traditional and the improved (with cryoprotectors) technology in order to obtain the additional index to compare. The results are presented in Figures 5 and 6.

We used our own improved technology [22] which contained the widened interpretations of sensory indices of the biological objects and the five-point scale to evaluate them. Because the appearance is considered the complex index which combines the shape, largeness, maturity grade, freshness, color of the berries and so on [10], we gave it the maximal meaning of the coefficient of weight – 0.35. Moreover, the application of any other criteria of evaluation in case of fruit and berries' disparity to the requirements of the appearance is believed to be inexpedient.

Figure 5

Mark evaluation of sensory indices of bilberries frozen by the traditional technology

Indices	Coefficient of weight	Points	Characteristics
Appearance	0.35	3	The berries are clean, evenly frozen; the small amount (up to 5 percents) is deformed with damaged peels; suitable for short-term storage (for one month)
Taste	0.2	2	The presence of well-expressed strange smack with further bitter after-taste
Color	0.1	3	The well-expressed discoloration with insignificant browning of the higher layer
Surface state	0.2	3	The shape of the berries is slightly changed; the small amount of squashed specimens (up to 5%), insignificant level of cracking with the signs of cellular juice leakage
Odor	0.15	4	The odor is natural without strange mixtures, slightly weakened in comparison with natural raw material

Figure 6

Mark evaluation of sensory indices of bilberries frozen by improved technology (with cryoprotectors)

Indices	Coefficient of weight	Points	Characteristics
Appearance	0.35	5	The berries are clean, evenly frozen, turgid, with bluish plaque, peels undamaged and shape kept; suitable for long-term frozen storage
Taste	0.2	5	Identical to natural fresh berries; without strange smacks
Color	0.1	5	Intensive, saturated, slightly amplified in comparison to fresh berries – evidently as the consequence of anthocyanine synthesis as the result of the chill stress
Surface state	0.2	5	Without damages, defects, cracks, changes in shape, and cellular juice losses
Odor	0.15	5	Immanent to fresh berries, but more intensive due to the synthesis of odorants as the result of the chill stress

The results of the experiments showed that bilberries frozen by the traditional technology had not gotten the maximal mark by any of the sensory index; according to our own elaborated recommendations, they are suitable only to short-term (one month) storage. Therefore, they should not be used in winter-and-spring period (with absence of fresh fruit and berries) as the source of vitamins and other valuable components.

On the contrary, bilberries frozen with cryoprotectors had gotten the maximal 5 points by all of the sensory indices; consequently, they had the status of the reliable source of vitamins and mineral elements (in the inter-seasonal period until the new harvest) confirmed.

The increase of the quality of frozen berry half products and the achievement of high sensory indices are the results of the ability of the researched cryoprotectors to lower the amount of frozen water. Correspondingly, the decrease of the number of ice crystals (which are the main factor of cryogenous damages of plant cells) benefits the formation of small-crystal glacial structure. According to the authors [9], such structure is different by its weak strength fields, which would essentially reduce the grade of mechanical destruction of cytoplasm substances and cellular membranes, and, subsequently, retain their holity during freezing, frozen storage, and defrosting.

Conclusions

1. Protection of the berries to freeze with all of the researched cryoprotectors allowed accomplishing one of the most important tasks for novel food technologies – to minimize the ruining action of minus temperatures. As the consequence, we could retain over 70 percents of ascorbic acid in frozen berries after their 12-month frozen storage. Meanwhile, traditional freezing technologies (without cryoprotectors) permitted to keep

the ascorbic acid amount in frozen and defrosted berries on the level of only ca. 30 percents, relatively to this index in fresh berries.

2. The effects achieved are confirmed as the result of the action of the certain substances in cryoprotective complexes (water solutions, first of all) containing various organic and inorganic components – glucose, fructose, sucrose; citric, sorbic and benzoic acids; magnesium chloride. The positive effect of procession of berries by cryoprotectors before freezing may be explained, relying on theoretic knowledge about the protectors' impact on cellular suspensions, obtained in cryobiology. Likewise, we can affirm that the presence of cryoprotectors can change the physical-and-chemical properties, so that the subsiding influences of low temperatures during freezing get less pernicious for cellular structures of the berries processed beforehand. The usage of cryoprotective methods aimed at overtaking the disadvantages of the traditional technologies is the perspective trend of improvement of plant raw preservation with usage of artificial cold.

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Effect of high pressure and soy protein isolate combinations on the water holding capacity and texture of pork meat batters

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Abstract

Introduction. The used of high pressure and soy protein isolate combinations to emulsion meat products could improve the quality, water holding capacity, texture and increase product yield.

Materials and methods. Raw pork batters were prepared as follows: 400g pork meat, 80g pork back-fat, 70g ice water,10g NaCl; sample C2 had 10g soy protein isolate (2%); sample C3 - 20g soy protein isolate (4%). The vacuum packed batters were put into a high pressure vessel and were done with 200 MPa for 10 min at 10±2° C. The texture profile analysis of cooked pork batters were carried out using a texture analyzer. Low field NMR relaxation measurements were carried out according in the NMR probe of a Niumag Pulsed NMR analyzer.

Results and discussion. Compared with the C1, all the cooking yield of pork batters with various amount of soy protein isolate were increased significantly. The emulsifying activity of 11S globulins was much significantly improved at 200 MPa, that enhanced the water holding capacity of soy protein isolate. High pressure processing induced texture modifications have been used to affect myofibrillar proteins and their gel-forming properties, raising the possibility of the development of processed comminuted meat products. Over 200 MPa treatment, the protein extractability was decreased significantly in meat batters, and caused protein denaturation and/or aggregation, which limited their functionalities. The effects of relaxation time and peak ration of cooked pork batters by high pressure processing with different soy protein isolate were determined. There was three characteristic peaks in the cooked pork batters, which was named as T_{2b}, T_{21} and T_{22}, respectively. T_{2b} is assigned to water tightly associated to protein and macro-molecular constituents, the relaxation population centered at approximately 0-10 ms in the cooked pork batters. The relaxation population of T_{21} is centered at approximately 10–100 ms, which is a major component and considered to intra-myofibrillar water and water within the protein structure.

Conclusion. The result of low field NMR exhibited that the batters with soy protein isolate had less water out the cooked pork batter and free water. Overall, the 2% soy protein isolate addition could improve the water holding capacity and texture of pork batters treated by high pressure.

Introduction

The application of high pressure processing to modify the properties of meat and soy proteins, increase the water holding capacity and texture of cooked meat and soy proteins products. The used of high pressure and soy protein isolate combinations to emulsion meat products could improve the quality and lower the salt and fat content in the meat industry.

High pressure is a non-thermal technology that has been successfully applied to several meat products, and the applications of high pressure in food industry continue growing recently years [1,2]. The functions of high pressure in meat products contain the inactivation of microorganism and enzymes with minimal effects on flavor, color and nutritional quality [3-5]. Study [6] authors observed an increase in water holding capacity due to the interaction of high pressure processing and salt in pork meat batter, this may be because increasing sodium chloride causes increasing denaturation of muscle proteins in high pressure treated meat batters and favors the solubilization of proteins and the formation of a gel network that retains water and fat. Study [7] authors found that the textural properties of hardness, chewiness, springiness, cohesiveness and resilience were significantly ($P < 0.05$) increased at an interval of 100 MPa and 200 MPa, except the textural property of adhesiveness up to 200 MPa, but no changes of of hardness, chewiness, springiness and resilience were observed up to 300 MPa and 400 MPa. Study [8] authors showed that free SH content of soy protein isolate was significantly ($P < 0.05$) increased after high pressure treatment at 200 MPa. However, it is important to study the effect of high pressure processing on the food components, mainly proteins in the meat and soy to optimize the processing parameters to get high-quality products [9,10]. Soy protein isolate is a commonly useful vegetable protein in the meat industry, which has a good water and fat holding capacity, excellent gelling and structuring behaviour [11,12]. Some researchers have reported that added the soy protein isolate to meat batters could improve the water holding capacity, texture and nutritional quality. But few papers reported the effect of high pressure and soy protein isolate combinations on property of pork meat batter.

Therefore, the objective of the present study was to determine the water holding capacity and texture differences of pork meat batter which were produced by high pressure with soy protein isolate, and thereby to establish a method to obtain pork meat batter with desirable quality.

Materials and methods

Raw materials and ingredients

The *longissimus dorsi* of chilled pork (Moisture, 71.35±0.52%; protein, 22.57±0.37%; fat; 2.83±0.26%; pH, 5.63±0.02) were derived from the landrace (100±5 kg) which were slaughtered at the age of about 6 months provided by the Gaojin Group (China), and the temperature after slaughter 24 h was 2~4 °C. After removing of the visible connective tissue and fat, the pork meat was minced using a meat chopper with a 6 mm holes plate (MGB-120, Shandong Jiaxin Food Machinery Co., Ltd., China). Pork back-fat (90.21±0.56% fat) was purchased from a local meat market (Xinxiang, China), and also was minced using a meat chopper with a 6 mm holes plate. Soy protein isolate (91.32±0.83% protein) was provided by Shandong Soy Foods co., Ltd (China).

Prepared pork batters

Raw pork batters were prepared as follows: C1, 400g pork meat, 80g pork back-fat, 70g ice water,10g NaCl; C2, 400g pork meat, 80g pork back-fat, 70g ice water,10g NaCl, 10g soy protein isolate (2%); C3, 400g pork meat, 80g pork back-fat, 70g ice water,10g NaCl, 20g soy protein isolate (4%). The pork batters were produced by a bowl chopper (Stephan UMC-5C, Germany). Briefly, the 400 g pork meat was placed into the bowl chopper with 20 g NaCl. The mixture was chopped for 30s with 1/3 ice water, then the 80g pork back-fat, 10g/20g soy protein isolate 1/3 ice water was added and the chopping was continued for 30s. Finally, the remaining ice water was added and chopped for 60s. During the chopping processing, the meat batters were maintained at a temperature below 8 °C. The raw pork batters were then stuffed into 24 mm diameter polyamide casings (Xianyi casing Co., Ltd., Henan, China) using a sausage stuffer machine (Xiaojin Machinery Co., Ltd., Hebei Shijiazhuang, China) and linked every 160 mm. Finally, the batters were vacuum packed for subsequent pressure processing.

High pressure treatment

High pressure treatments of sausage batters were carried out in a 0.3 L capacity high pressure vessel (S-FL-850-9-W/FPG5620YHL, Stansted Fluid Power Ltd., Stansted, UK) which has a maximum pressure limit of 900 MPa and can work in the temperature range of -20ºC to +90ºC with a thermo-stated jacket (Figure 1). Product canister: 260mm internal usable height with demountable thermacouple, 37mm internal usable diameter [13].

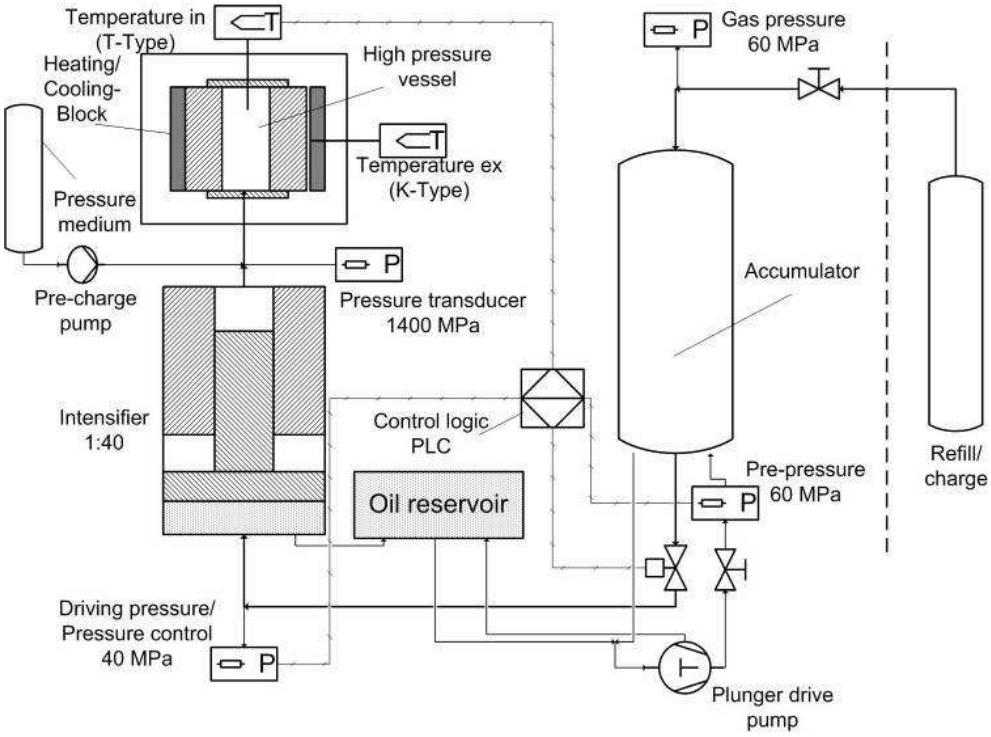

Figure 1. Schematic diagram High pressure vessel with heating cooling system (S-FL-850-9-W/FPG5620YHL, Stansted Fluid Power Ltd., Stansted, UK) [13]

The pressure transmitting medium used was water and was previously adjusted to the desired temperatures with circulating water from a thermo-stating circulator bath (ILB-WCS, STIK Shanghai Co., Ltd.). The temperature of the pressure medium was monitored during processing by a T-type thermocouple fixed inside the vessel. The temperature was maintained by circulation of the temperature controlled fluid through. The compression and decompression took place over a period of 42 s and 25 s respectively. The time spent on loading and unloading sample was approximately 1 min.

All samples were heated in a water bath (TW20, JULABO Technology Co. Ltd., Seelbach, Germany) at ambient pressure (0.1 MPa) if not specified.

The pork batters were done with 200 MPa for 10 min at 10±2 °C. All samples were heated in a water bath (HH-42, Changzhou Guohua Electrical Appliance Co., Ltd., China) at 80 °C for 30 min (internal temperature 72 °C), then cooled immediately with running water and stored at 4 °C for analysis.

Determination of cooking yield

The cooking yield of pork batters was calculated according to the following formula [14]:

$$Cooking\ yield\ (\%) = cooked\ meat\ batter/raw\ meat\ batter \times 100\%$$

Each measurement was replicated 5 times.

Water holding capacity

The water holding capacity of the samples was measured according to the method of [15]. Sample with casing was weighed (weightsample). After removing the casing from the sample, the surface water of the product was absorbed using filter paper and reweighed ($weight_{product}$). The empty casing was dried and weighed ($weight_{casing}$). Released water was expressed as a percentage of the original weight.

$$Released\ water\ (\%) = $$
$$=(weight_{sample} - weight_{product} - weight_{casing})/(weight_{sample} - weight_{casing}) \times 100$$

Determination of texture

Samples were assessed for texture profile analysis (TPA) according to the procedure of [16-18], using a texture analyzer TA-XT plus (Stable Micro Systems Ltd., UK) with an aluminum cylindrical probe P/36R at ambient temperature (20 - 25°C). The indicators of hardness, springiness, cohesiveness and chewiness were determined. Each measurement was replicated 5 times.

Parameters as follow: pre-test speed 2 mm/s, test speed 2 mm/s, post-test speed 2 mm/s, compression ratio 40 %, trigger force 5 g, and 5 s was allowed between the two compression cycles.

The texture profile analysis of cooked pork batters (the cylindrical-shaped with a diameter of 20 mm and a height of 20 mm) were carried out using a texture analyzer (TA-XT plus Texture analyzer, Stable Micro Systems, UK) with an aluminum cylindrical probe P/36R.

Cylindrical samples (20 mm diameter; 20 mm height) were axially compressed to 40 % of their original height using a double compression cycle test. The trigger force used for the test was 5 g, with a pretest speed of 2 mm/s, test speed 2 mm/s, post-test speed 2 mm/s. A time of 5s was allowed to elapse between the two compression cycles. The data were generated by Exponent software (Exponent stable microsystem, version 5.1.2.0, Stable Microsystems Ltd., UK) provided with the instrument (Figure 2). Attributes of hardness, springiness, cohesiveness, chewiness and resilience were determined. Each measurement was replicated 5 times.

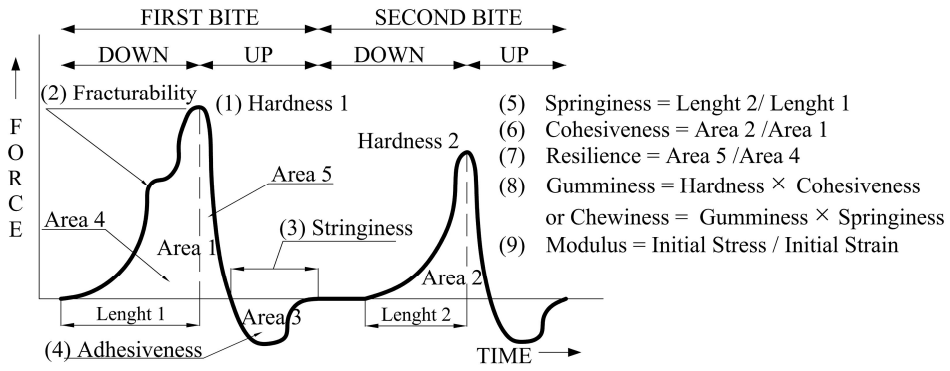

Figure 2. The parameter definition interpretation of qualitative curve analytical method [16]

Hardness. It is the biggest peak of compression for the first time.

Springiness. The quotient or volume ratio of the compressed deformed sample to the predeformed condition after removing the deforming force. Elasticity is expressed by the ratio (Length2/ Length1) of the specimen recovery height (Length 2) measured in the second compression to the first compression deformation (Length 1).

Cohesiveness. The relative resistance of the test sample to the second compression after the first compression deformation is shown in the curve as the ratio of positive work (Area 2/Area 1) of the two compressions. This value represents the total work required to overcome the attraction between the two surfaces when the probe comes into contact with the sample.

Chewiness. It is only used to describe the test sample in solid state, indicating the energy required to chew the solid sample into a stable state when swallowing. The numerical value is expressed by the product of the stickiness and elasticity (hardness x cohesive elasticity).

Low field NMR measurements

Low field NMR relaxation measurements were carried out according to the method of [19, 32]. About 2 g of the cooked pork batter was placed in a 15 mm glass tube and inserted in the NMR probe of a Niumag Pulsed NMR analyzer (PQ001, Niumag Electric Corporation, Shanghai, China).

Spin-spin relaxation time (T_2) was measured made a τ-value of 350 μs by the Carr–Purcell–Meiboom–Gill sequence at resonance frequency of 22.6 MHz, 32 °C. Post processing of T2 data distributed exponential fitting of Carr-Purcell-Meiboom-Gill decay curves were performed by Multi-Exp Inv Analysis software (Niumag Electric Corp., Shanghai, China). Each measurement was replicated 4 times.

Statistical analysis

The experiment was four replications. The data was analyzed using the one-way ANOVA program (SPSS v.18.0 for Windows), the difference between means was considered significant at $P < 0.05$.

Results and discussion

Cooking yield

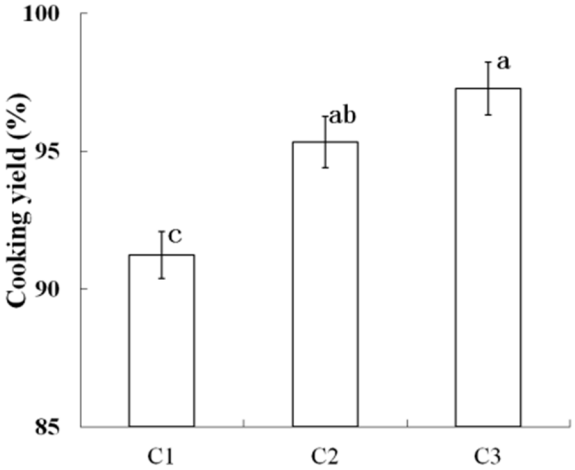

Figure 3. Effect on cooking yield (%) of pork meat batters by high pressure processing with different soy protein isolate:
C1, 0g soy protein isolate; C2: 10g soy protein isolate; C3: 20g soy protein isolate.
Each value represents the mean ± SD, n = 4.
[a-c] Different parameter superscripts in the figure indicate significant differences ($p < 0.05$)

The effect of high pressure with various amount of soy protein isolate on the cooking yield of pork batters was shown in Figure 3. A higher cooking yield of pork batters reflects a better water holding capacity. Compared with the C1, all the cooking yield of pork batters with various amount of soy protein isolate were increased significantly ($P < 0.05$), but the cooking yields of C1 and C2 were no significantly ($P < 0.05$) differences. The reason might be that added the 2% soy protein isolate could hold the water of pork batters very well, so increased the soy protein isolate addition could not improved the cooking yield. The emulsifying activity of 11S globulins was much significantly improved at 200 MPa, that enhanced the water holding capacity of soy protein isolate [20]. Study [21] authors used of the soy protein isolated, wheat flour (WF), and κ-carrageenan as binder, showed that the addition of binders improved water-binding properties of pressure or non-pressure-induced restructured pork. The similar result was reported by [22], who used the dried egg white as fat replacement to obtain a low-fat chicken gel by means of high pressure, the water binding properties and hardness were improved, suggested their participation in the network structure coupled to the myofibrillar proteins, and noted that the modifying certain functional characteristics of chicken meat gels with low fat content by means of high pressure and the addition of dried egg white. Thus, the addition of soy protein isolate could improve the cooking yield of pork batters.

Texture

Table 1
Texture of cooked pork batters by high pressure processing with different soy protein isolate

Sample	Hardness (N)	Springiness	Cohesiveness	Chewiness (N mm)
C1	47.32±1.12^{c}	0.837±0.008^{b}	0.641±0.005^{c}	27.05±0.85^{c}
C2	53.21±0.98^{a}	0.863±0.009^{a}	0.687±0.007^{a}	35.68±0.89^{a}
C3	50.42±1.05^{b}	0.835±0.007^{b}	0.655±0.008^{b}	29.67±0.96^{b}

C1, 0g soy protein isolate; C2: 10g soy protein isolate; C3: 20g soy protein isolate.
Each value represents the mean ± SD, n = 4.
$^{a-c}$ Different parameter superscripts in the figure indicate significant differences ($p < 0.05$).

The texture of cooked pork batters were affected significant ($P < 0.05$) by high pressure and soy protein isolate combinations (Table 1). Compared with the C1, all the hardness, springiness, cohesiveness and chewiness of pork batters with various amount of soy protein isolate were increased significantly ($P < 0.05$), except the springiness of C3. Compared with the 4% (C3), the hardness, springiness, cohesiveness and chewiness of pork cooked batter with 2% soy protein isolate (C2) were significantly increased ($P < 0.05$). High pressure processing induced texture modifications have been used to affect myofibrillar proteins and their gel-forming properties, raising the possibility of the development of processed comminuted meat products. Over 200 MPa treatment, the protein extractability was decreased significantly in meat batters, and caused protein denaturation and/or aggregation, which limited their functionalities [23,24]. Although the soy protein isolate have has a good water and fat holding capacity, excellent gelling and structuring behaviour, some paper have reported that excessive added the soy protein isolate could lower the texture of meat batters [21]. Therefore, the pork cooked batter with 2% soy protein isolate (C2) had the best texture.

Low field NMR

The effects of relaxation time and peak ration of cooked pork batters by high pressure processing with different soy protein isolate were determined (Table 2). There was three characteristic peaks in the cooked pork batters, which was named as T_{2b}, T_{21} and T_{22}, respectively. T_{2b} is assigned to water tightly associated to protein and macro-molecular constituents, the relaxation population centered at approximately 0-10 ms in the cooked pork batters 25[19]. The relaxation population of T_{21} is centered at approximately 10-100 ms, which is a major component and considered to intra-myofibrillar water and water within the protein structure. T_{22} is corresponds to extra-myofibrillar water and centered at approximately100-400 ms [26,27] Compared with the C1, the initial relaxation times of T_{2b}, T_{21} and T_{22} were quicker ($p < 0.05$) in the C2 and C3, the result indicated that the cooked pork batters made with various amounts of soy protein isolate were bound tightly, because the changes of fast relaxing protein and slowly relaxing water protons [28,29].

These also were accordance with the changes of texture and cooking yield (Table 1 and Figure 3). The reason was possible that the soy protein isolate had excellent gelling and structuring behaviour, then a better gel structure of cooked pork batters by high pressure processing was formed when added the soy protein isolate [30]. The emulsifying activity of

11S globulins of soy protein isolate was much significantly improved at 200 MPa, through the changes of protein solubility, surface hydrophobicity, free SH content and secondary structure [20,31]. All the peak rations of T_{2b} were no significant differences ($p > 0.05$), C2 and C3 had the smallest peak rations of T_{22}, and had the largest peak ration of T_{21} (Figure 4).

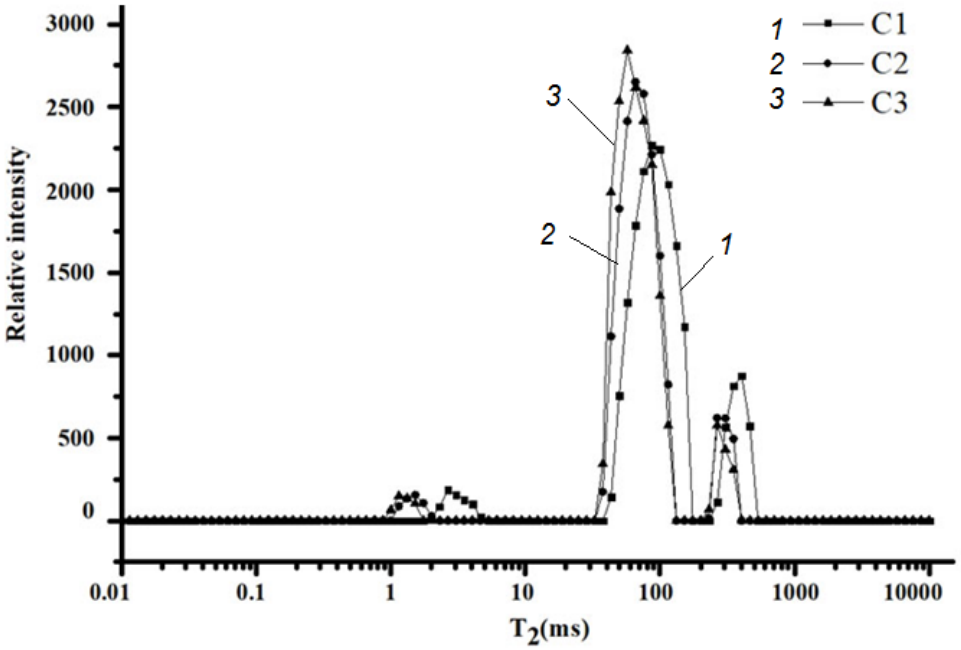

Figure 4. Curves of relaxation time (T2) in cooked pork batters by high pressure processing with 1000 different soy protein isolate

Added the soy protein isolate and high pressure processing combinations could increase the protein content, more meat proteins can become available for gel formation of the meat matrix. These caused the water tightly associated to protein and macromolecular constituents decreased, and improve water holding capacity of cooked meat batters [33]. Therefore, added the soy protein isolate increased the water holding capacity, and improved the texture of cooked meat batters.

Table 2

Relaxation time (ms) and peak ration (%) of cooked pork batters by high pressure processing with different soy protein isolate

Sample	Relaxation time (ms)			Peak ration (%)		
	T_{2b}	T_{21}	T_{22}	T_{2b}	T_{21}	T_{22}
C1	1.95±0.13^a	44.23±1.42^a	265.51±4.26^a	1.22±0.15^a	85.66±2.36^b	13.26±0.85^a
C2	1.12±0.15^b	37.25±1.59^b	232.87±4.68^b	0.96±0.12^a	91.87±2.45^a	8.31±0.80^b
C3	1.06±0.11^b	36.30±1.45^b	227.52±4.31^b	1.03±0.12^a	93.26±2.14^a	7.03±0.86^b

C1, 0g soy protein isolate; C2: 10g soy protein isolate; C3: 20g soy protein isolate.
Each value represents the mean ± SD, n = 4.

Conclusion

The effect of high pressure and soy protein isolate combinations on the gel properties of pork batters was significant differences ($P < 0.05$). Compared with the C1, C2 and C3 had a higher cooking yield and hardness, cohesiveness and chewiness. The result of low field NMR exhibited that the batters with soy protein isolate had less water out the cooked pork batter and free water. Thus, C2 had the best water holding capacity and texture. Overall, the 2% soy protein isolate addition could improve the water holding capacity and texture of pork batters treated by high pressure.

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Determination of the shelf life of smoked sea bass (*Dicentrarchus labrax* linaeus, 1758) marinade stored under refrigerated conditions (4 °C)

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Abstract

Introduction. In this study, two different marinade (plain and smoked) were prepared with seabass and determination of their shelf-life was aimed by investigating the quality according to organoleptic, chemical and microbiological parameters.

Material and methods. Fishes supplied from an aquaculture facility were brought to the laboratory under cold storage and filleted after cleaning process. First group (Group A: Plain) was put into the marination solution (Fish:solution ratio was 1:2, 1.68% alcohol vinegar, 6.4% salt and 0.01% citric acid) for 5 days. In second group (Group B: Smoked) fish were smoked and air cooled to the ambient temperature. Cold fish fillets were waited in the marination solution (Fish:solution ratio was 1:2, 1.2% alcohol vinegar, 5.5% salt and 0.01% citric acid) for 2 days.

Result and discussion. According to the results in terms of the chemical analyses, while TBA value was determined as 0,26±0,01 mgMDA/kg in raw material, at the end of the study this value was determined as 4,38±0,05 mgMDA/kg in Group A (5th month) and 3,05±0,02 mgMDA/kg in Group B (7th month). According to results in terms of the microbiological analyses, TMAB count was determined as 2,00±0,04 CFU/g in raw material but total bacteria and yeast-mold count was remained <10 CFU/g during the storage period. Coliform bacteria were not encountered in the study. For the organoleptic analyses 5 experienced panelists evaluated the products according to colour, odour, texture, flavour and general appreciation. Both groups got high scores in the beginning but Group A got low scores in 5th month and Group B had low scores in 7th month from panelists and lost quality.

Conclusion. As a result, smoked sea bass marinade was appreciated more than plain sea bass marinade and the shelf life of smoked marinade was detected higher than the plain marinade.

Introduction

Fish, which is essential for human health and contains a wealth of fatty acids, is a must consume food source for the sake of a healthy and high quality life. EPA and DHA fatty acids are known to have good use for human health. It's stated that, fish consumption has a positive effect on many illnesses like cardiovascular diseases, development of brain and intelligence, strengthening the immune system, hypertension, cholesterol, depression, amnesia, etc., an even various disease may occur when the lack of consumption [1,2] Seabass (*Dicentrarchus labrax* Linaeus, 1758), which has a high nutrition value, is naturally found in seas around Turkey; besides it has been cultivated with great numbers in recent years. Total amount of sea bass production that has white meat, delicious taste and low fat content was 80.847 tones [3]. One of the most cultivated fish species in Turkey is seabass and not only it is consumed fresh; but it is exported frozen or processed as well.

With processing seafood, many products are on the market and alternatives are being created on fish consumption lately. Marinated products are on demand along with dried, smoked, salted and canned ones. Marinated products are generally processed by a seasoning process with certain amount of salt and acedic acid brine within a certain time. Ripening process in marinates is resulted from opposing influence of salt and acedic acid on fish meat. Salt provides toughness for fish meat; whereas, acid does smoothness. The ripened fish after a certain period is put into marinade containers and assorted sauce, oil, etc., are added on [4]. Then again shelf life of marinades may alter according to the factors like fish variety, acid/salt rate of brine, brining period and storage conditions. Salt and acid have an effect on decreasing bacteria and enzyme activities so shelf life extends [5]. On the other hand, shelf life of marinades can also be as short as 4-5 months due to the factors like organoleptic changes, rancidity and putrefaction [6]. As for smoking process; it expresses a number of methods in order to give fish a different color, smell, taste or flavor. In this context; first of all, the fish is steeped into salty water solution. After that it is smoked into a special oven. The product is dehydrated with the help of salting and drying; it is also made use of antimicrobials and antioxidants' conservativeness on the compound of smoking process [7-10]. Besides having positive effect on shelf life, smoking process provides high acceptability in view of sensitivity. A product is featured in sensitivity thus attracts the attention of customers especially in developed countries [11]

Either of them are fish conservation methods which have been widely used for long in fishery processing technology. In this research an outcome was tried to obtain by using both of the different technologies. Also in this study it is tried to determine the shelf life of seabass, which was marinated in two different methods (plain and smoked), and aimed to analyze the quality changes during stockpiling.

Material and method

100 Seabass (*Dicentrarchus labrax* Linaeus, 1758) whose approximate lengths are 28.53±0.12 cm and weights are 277.35±2.45 g were brought to laboratory to under cold storage and these fish were supplied from Kuzey Su Ürünleri Fish Farm which is situated between Samsun-Sinop provinces in December 2017. After removing guts, beheading and cleaning, they were filleted without scaling. Before the process, fillets were steeped into the icy salted water (20%, 30 mins) until emptying their blood, later that they were washed off in order to leak all the extra water. All the fillets were divided into two groups. The first fillets

group (Group A) was plain marinated bass and the other group (Group B) was hot smoked. In order to maturing fish; a solution which is derived from diluting industrial marinade brine was used. On the other hand, smoking process was completed in semi traditional smoking oven in Sinop University Faculty of Fisheries Processing Laboratory using wood shavings by beech tree.

Fish processing

For plain seabass marinade (Group A), the fish was stored for 6 days in refrigerator circumstances. The rate of fish to brine is 1/2 and the brine consists of 1.68% alcohol vinegar, 6.4% salt and 0.1% citric acid. At the end of marinating, the fish were taken out of brine and were put to draining.

For second group (Group B) marinade; the fish was aligned onto baking trays then smoked. Smoking oven was adjusted to 60°C and the fish was kept in smoking oven for 45 min. as 20 min. pre-drying and 25 min. smoking process. After smoking process ends, the wish was taken to a colder place to cool off. After that it was put into marinade brine (F:B=1/2, 1.2% alcohol brine+5.5% salt+0.1 citric acid) and kept for 3 days in refrigerator. After the maturing process; the fish in both groups was aligned into marinade containers. Then the containers were filled with sunflower oil and covered. Consequently, the marinades were all stored in refrigerator.

Analyzing methods

The study was executed as 2 groups; on the other hand, executed as 2 recurrence analyses and 2 parallel analyses. During storage period the products' qualities were examined also it was tried to figure out the shelf life in refrigerator circumstances by the help of monthly sensory, chemical, physical and microbiologic analysis.

TVB-N amounts of fresh samples and products were modified by Antonacopoulus and determined by Lücke-Geidel method [12]. Quality classification of fish in TVB-N value was done according to Varlık et al. [13]. Amount of TBA was done according to Erkan and Özden [14]. Quality of fish in TBA value was evaluated according to Varlık et al [13] and determination of salt and vinegar was made according to Varlık et al. [15]. In pH measurement the fish was added into pure water as 1:1; then, measured with WTW Multi 340i portable pH-meter probe [16]. Color was analyzed with Minolta "CR-400 Chromometer" brand device according to CI L* a* b* scale and values were given as L* a* b*. White platform of the device was used for calibration [17]. Water activity was measured in Novasina brand automatic water activity measurement device.

The microbiologic analyses are bacterial counts which are total mesophilic aerobic bacteria, total psychrophile aerobic bacteria, yeast-mold bacteria and total coliforms. The exterior surfaces of packages were cleansed with %70 ethyl alcohol then opened with sterilized knife. 10 grams of fish samples were taken into stomacher bags with sterilized spatula and homogenized with adding in 90 ml peptone solution near the flame [18]. 10^{-1}-10^{-6} rated dilutions were prepared using 1ml homogenization and 9ml physiological salty water solution (%0,85 NaCl). Plate Count Agar was used in order to count the total mesophilic aero and psychrophile bacteria. The fish was incubated at 37°C for 2 days for petris mesophilic count and at 7°C for 10 days for psychrophile bacteria count in microbiologic analysis which was made with pour plate technique [19].

All colonies that were observed in petri was regarded as "total bacteria" and counted standardly; then, the result was given as LogKOB/g at the end of the incubation [20]. PDA

(Potatos Dextroz Agar) feedlot was used for yeast and mold counting. In the pour plate technique analysis, yeast-mold number was counted and specified after 3 days of incubation at 28°C and the results were given as LogKOB/g [13,21,22]. VRBA (Violet Red Bile Agar) (Lab M 31) feedlot was used for total coliform bacteria counting. Petri boxes were turned upside down then incubated for 1 day at 35°C after feedlots were frozen [21]. A group of 5 experienced panelists were chosen for sensory analysis and they were given forms in order to evaluate the products. The sensory evaluation form was modified according to the chart, which is expressed for marinated products, notified by Varlık *et al* [13] and used by Schormüller [23]. The products were evaluated by giving them ranks between 0-5 from the points of color, smell, taste, texture and general liking (0-1: inconsumable, 1-2: Bad, 2-3: Nat bad, 3-4: Good, 4-5: Very good) and those which ranked under 2 points were specified as inconsumable.

Medians and standard errors of the results were analyzed by one-way analysis of variance and tukey's test with the help of Microsoft Excel 2010 and Minitab 17 packaged software [24].

Results and discussion

Now that the products keep their chemical and microbiologic quality during storage period, shelf life of them was determined by sensorial perception. The beginning of the experiment expresses the first day of study while the end it expresses the 5th month for Group A (plain seabass marinade) and 7th month for group B (smoked seabass marinade).

Chemical and physical analysis results

The TVB-N, TBA, pH analyses results and water activity(aw) values of both samples were given in Figure 1. In the present study, TBA value of fresh samples were found as 0.26±0.01 mg MDA/kg. After marination of fresh samples, A and B groups were also examined with regard to TBA values. Due to the applied long time marination process to group A, Fish oils were partially degradation and the TBA value was determined as 3.52±0.09 increasingly in this group at the end of the marination process. In group B, due to the antioxidant effect of smoke compounds TBA value of group B showed less increased than group A and it determined as 1.61±0.13 mg MDA/kg.

During storage time, it was observed that there were increases for both groups but it was also detected that this increase could not surpassed over 7-8 mg MDA/kg value which is the minimum consumable rate. The value differences between the groups were found significant both for the beginning and the end of the study ($p<0.05$).

The change of fat rancidity depending on time was examined with TBA analysis. The analysis results were evaluated by considering the criteria that were displayed by Schormüller [25]and were stated by Varlık et al. [13]. Baygar et al. confirmed in his study that TBA value of crude material as 0.30 while the value of material in marinate (that is scaled) as 4.25 mg MDA/kg [26]. Alparslan et al. stated that seabass marinade did not exceed 8 mg MDA/kg which is the highest consumable limit at the end of 90 days of storing period [27]. Likewise, Kaya detected that seabass marinade did not exceed the limit of TBA value during 200 days of storing period [28].

Balıkçı observed that TBA value of both plain and dill added smoked mackerel marinade increases during 9 months of storing time though the value kept under specified limits [29]. Günlü stated that TBA values of products increase when he examined the quality changes of

seabass after smoking; however, none of the party's TBA value exceeds the consumable limit during storing period [30]. The results are compatible with present study. The reason is Group A spent more time in maturing brine; thus, there was more deterioration of fat. It could also be said that the reason why Group B has less TBA value during storing period was originated from smoking process. Goulas and Kontominas indicated in their study on mackerel that in the course of storing, the low value of TBA is caused by phenolic matters in smoke compounds and these matters have anti-oxidative effect [31].

According to TVB-N analysis, TVB-N value of fresh seabass was determined as 17.11±0.28 mg/100g and this TVB-N value was identified as 11.66±0.44mg/100g for group A, 9.97±0.33mg/100g for group B after marination proces decreasingly. The reason for this decrease in TVB-N values can be said that to be the decrease in the pH value due to fish meat waits in brine water.

Since both marinate groups partially lost their acidic properties over time, TVB-N values increased somewhat in both groups at the end of the experiment and TVB-N values of Group A and Group B were determined as 17.41±0.17, 17.63±0.22mg/100g respectively. The difference between two groups was found significant ($p<0.05$).

One of the analyses which is considered a freshness indicator of seafood is TVB-N analysis. The results were evaluated by regarding the criteria like; samples containing 25mg/100g TVB-N as "very good", 30mg/100g TVB-N as "good", 35mg/100g TVB-N as "marketable", and samples containing more than 35mg/100g TVB-N as "spoiled" [13]. Baygar et al., found the TVB-N value of fresh sample as 16.89 mg/100g, and stated that the sharp fall of TVB-N amount was caused by pH decrease which was affected from acetic acid used in the brine [32]. Kaya, stated that TVB-N value of fresh seabass as 15.24±0.02mg/100g decreases down to 13.12±0.58 mg/100g for plain marinades on marination day, 13.33±0.11 mg/100g for sauced marinades; he also stated that these values do not exceed the consumable limit rates in time [28]. Present study shows similarity to previous researchers' results.

In present study, pH value of fresh seabass was measured as 6.47±0.01. After marination process, pH value of Group A and B were determined as 4.17±0.02 and 4.38±0.03 respectively resulting from acidic treatment.

pH value of fresh fish is expected to be between 6-6.5 with the changes depending on the specie, size, season and rigor mortis [13]. Kaya, determined the fresh seabass pH value as 6.04 ± 0.04 [28], whereas Taşkaya et al. determined as 6.45. pH interval of marinated products is very significant [33]. pH interval is supposed to be between 4-4,5 for marinated products [5,13]. Therefore, it is important both to prevent bacterial growth and to emerge some flavoring matters. Likewise, Alparslan et al. detected the fresh pH value as 6.35 for seabass while marinated product's pH value was as 4.32 [27].

Kaya, measured the beginning pH value of plain seabass marinade as 3.83±0.05 while Çakır; found the beginning pH value of anchovy marinade as 3.75 [28,34]. Seeing that the acid rate that researchers used at their researches is more, those pH values are below from present study. Most researchers stated that the beginning pH values are between 4-4.8 for marinated products [32,35,36]. Even though the research results share similarity to present study, it is considered that the low rate of acid in the brine affected pH value.

When the water activity is investigated, the values which were measured for Group A and B found respectively as 0.932±0.002 and 0.921±0.001 at the beginning of the experiment and as 0.940±0.001 and 0.931±0.001 at the end of the experiment; the differences between them were found significant ($p<0.05$).

Işıdan detected the a_w value of fresh fish in his shad marinade as 0.995±0.001 but it was 0.953±0.001 at the beginning of the experiment [37]. Giuffrida et al., detected that a_w value of his seabass marinade decreased after marinating and during storing time [38]. Previous

researches indicate increases in a_w value for the products originating from the water holding capacity of salt; so the results show similarity to present study.

As it is known, a_w values decreased due to brine and smoking effects so the water, which is necessary for microorganism growth, removed partially. On the contrary, Huss et al., stated that falling of a_w value, along with pH, restricts or stops bacterial growth after marinating [39].

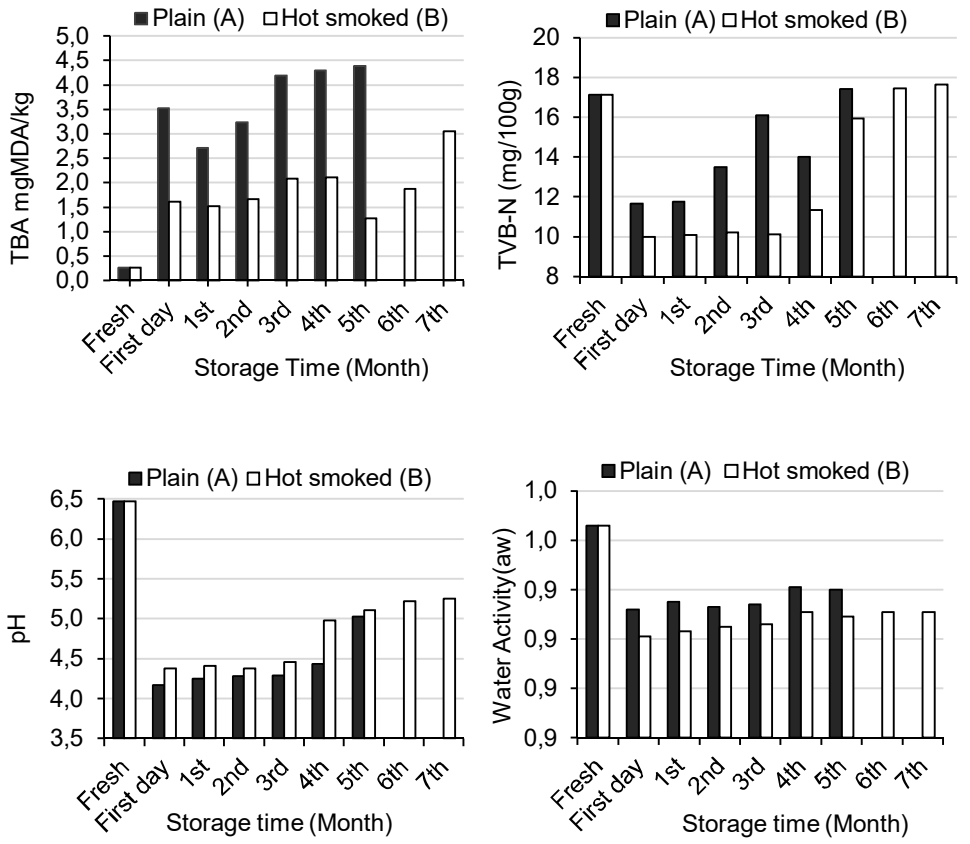

Figure. 1. The TVB-N, TBA and pH analysis results and water activity values of group A and group B

Monthly analyses were conducted in order to determine the percent of salt and percent of vinegar (total acidity) in fish meat. The salt and percent of vinegar (total acidity) analyses results in sea bass marinade samples were given in Figure 2.

After marination process, Salt and vineagar contents of Group A and B increased to %3.73±0.17, %3.02±0.05 and %1.03±0.01, %0.86±0,01 respectively ($p<0.05$). As the marinated samples lost their water during storage, it was observed that salt content increased and as the marinated samples waited in package with oil, vinegar content declined in both groups.

Also, in which there were irregular rises and falls of acidity-salt values, it is considered that keeping the fish in brine before process as well as the acidity-salt rate in the maturing brine could affect these values. Smoked product's being low in acidity and salt values than Group A can be caused by smoking process in addition to the reason above

When salt amounts were examined both for Groups A and B on the last day of the experiment, they were detected as %4.00±0.02, %3.45±0.03 respectively, As of vinegar amounts were detected as %0.60±0.03, %0.43±0,02 respectively. The difference between them was found statistically significant ($p<0.05$).

Kaya, detected the beginning value of acidity and salt of seabass marinade as %1.97±0.12 and %5.09±0.04 and also stated that those values declined on account of time [28]. Çakır, detected the beginning (control) value of acidity and salt for anchovy marinade in plastic container respectively as %4.50±0.02 and %0.85±0.01 he also stated that there were irregular increases in acidity and salt values because of time [34].

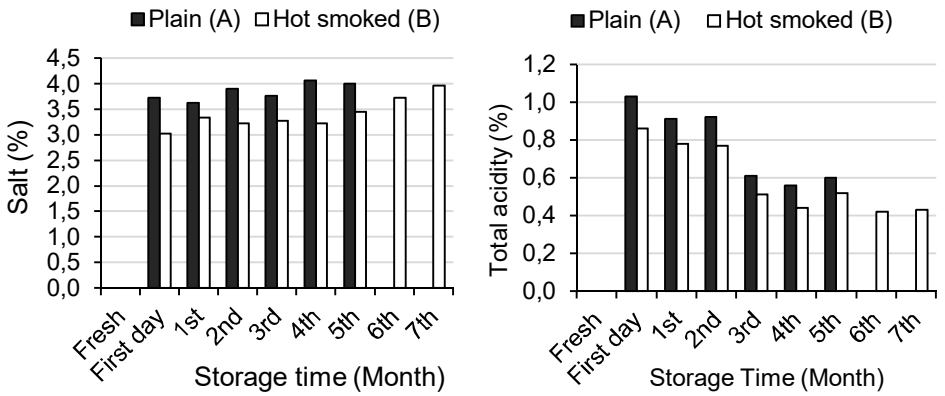

Figure 2. Salt (%) and total acidity (%) analysis results of group A and group B

The color analysis results were given in Table 1. The quantitative differences of changes in products' physical appearances were revealed with color analysis. Each value (L*, a*, b*), which was measured in the device, reveals a different color notion and the changes during storing. When the results which were acquired by the measurements from 2 different spots of fish fillets were examined and L* (brightness) value of fresh fish was determined as 41.43±1,23. L* values of Group A and B were determined respectively as 78.50±0.58 and 67.36±0.81 on the first day of the experiment ($p<0.05$). The reason might be the decolorizing feature of acid in the ripening brine.

a* value is 1.64±0.45 in fresh sample and it was found at the beginning of the experiment as -3.58±0.24 for Group A and as 4.87±0.49 for Group B ($p<0.05$). While b* value of fresh fish is -3.16±0.38, this value is detected at the beginning of the experiment as 2.64±0.70 for Group A and 24.84±0.59 for Group B. The measured a* and b* values were higher for both groups than fresh sample, in other words it was observed that there were changes in product color. Especially, emerging highly positive of b* (24.84±0.59) value which was measured in Group B proved that the product was yellowish which is desired to be so for smoked products. This proves that the smoke demonstrably affects the color. The differences between two groups was found significant ($p<0.05$).

L* (brightness) value is measured between 0-100 and it expresses the color of a product is getting from dark to light as it gets closer to 100. a* value, which is measured in coloring device, is depicted by greenish color when it is negative; whereas it is depicted by reddish color when it is positive. b* value is depicted by bluish color when it is negative; whereas it is depicted by yellowish color when it is positive.

Bilir, measured the beginning L*, a* and b* values respectively as 41.63, 0.64 and 9.8 and detected that L* value increases, a* value comes out positive, and b* value is higher for fish meat after ripening, in his marinade study made by sardine [40]. Kadak, calculated the fresh L* value as 40.01, a* value as 0.29, and b* value as 9.14 of chitosan added anchovy marinade. He found these values on the first day when he marinated the fish respectively as 63.65, 1.71, and 12.22. These changes in fish meat are accordant with the data of present study [41].

Table 1

Color analysis results of group A and group B

Storage time (Month)		A	B
Fresh Fish	**L***	41.43 ± 1.23^{Aa}	41.43 ± 1.23^{Aa}
First day		78.50 ± 0.58^{Abc}	67.36 ± 0.81^{Bb}
1st		75.11 ± 0.96^{Ac}	71.76 ± 0.55^{Bc}
2nd		76.92 ± 1.23^{Ac}	72.98 ± 1.04^{Bc}
3rd		78.34 ± 0.44^{Abc}	69.88 ± 0.53^{Bbc}
4th		82.22 ± 0.24^{Ab}	69.73 ± 0.30^{Bbc}
5th		67.52 ± 1.29^{Ad}	62.75 ± 0.24^{Bd}
6th		-	58.82 ± 1.45^{e}
7th		-	60.13 ± 0.31^{de}
Fresh Fish	**a***	1.64 ± 0.45^{Aa}	1.64 ± 0.45^{Aa}
First day		-3.58 ± 0.24^{Abd}	4.87 ± 0.49^{Bbc}
1st		-3.61 ± 0.13^{Abd}	3.72 ± 0.34^{Bcd}
2nd		-1.05 ± 1.15^{Ac}	1.24 ± 0.44^{Aa}
3rd		-1.45 ± 0.24^{Abc}	2.58 ± 0.2^{Bad}
4th		-3.24 ± 0.11^{Abcd}	4.93 ± 0.07^{Bbc}
5th		-3.92 ± 0.29^{Ad}	4.10 ± 0.23^{Bbcd}
6th		-	5.68 ± 0.60^{b}
7th		-	5.16 ± 0.16^{bc}
Fresh Fish	**b***	-3.16 ± 0.38^{Aa}	-3.16 ± 0.38^{Aa}
First day		2.64 ± 0.70^{Abc}	24.84 ± 0.59^{Bbc}
1st		1.00 ± 0.49^{Ac}	23.70 ± 0.81^{Bc}
2nd		4.97 ± 0.81^{Abd}	23.91 ± 1.04^{Bc}
3rd		6.90 ± 0.35^{Ad}	27.17 ± 0.33^{Bb}
4th		9.28 ± 1.03^{Ad}	24.60 ± 0.19^{Bbc}
5th		5.62 ± 0.74^{Abd}	23.28 ± 0.33^{Bc}
6th		-	24.09 ± 0.47^{c}
7th		-	25.26 ± 0.20^{bc}

Values with different letters in the row (→) (A, B,…) and in the column (↓) (a, b,…) differ significantly ($p<0.05$).
A: Plain sea bass marinade
B: Hot smoked sea bass marinade.

Microbiological analysis results

In present study, the products' monthly Total Mesophilic Aerobic Bacteria, Total Psychrophilic Aerobic Bacteria, Total Coliform Bacteria and Total Yeast-Mold Bacteria Loads were examined. According to the microbiological analysis results, the total mesophilic bacteria number was detected as 2.00±0.04 LogCUF/g; however, not a single bacterial reproduction was observed during storing time (<10CUF/g). Due to the lethal effect of the smoke on the bacteria and the preventing effect of the marination process on the growth of bacteria, The microbiological load remained below the limit values.in the study. Coliform group bacteria were not detected at present study**.**

Kaya, examined the products in seabass marinade microbiologically during storing time (200 days), and hereby he stated that the products did not exceed the consumable limit (10^6 CUF/g) [28]. Balıkçı, reported that smoked mackerel marinade did not exceed the limit value of total mesophilic aerobic bacteria count during storing time and he also stated that this prevents the bacterial growth as a result of marinating and smoking processes [29].

Sen and Temelli, stated that they marinated anchovy and microorganism count decreased after marinating [42]. Kılınç and Çaklı, reported that yeast and mold growth was not observed in tomato sauce marinated sardine and also Olgunoğlu reported the same for marinated anchovy [43,44].

Sensory analyses results

At present study, in which the quality of seabass marinade under refrigerator conditions examined, shelf life of the product was determined as a result of sensory analyses and these results were given in Figure 3. At first, the products in both groups with high ratings were liked and consumed by panelists. A difference was detected between groups owing to the storing time. Group A at the end of 5^{th} month and Group B at the end of 7^{th} month got low ratings from the panelists and lost their qualities. Throughout the study, unpleasant changes in the color and smell of the product were not noted; on the other hand, it was stated by the panelists that some deterioration occurred in the texture and the taste disappeared in the 4^{th} month for Group A and in the 6^{th} month for Group B. Therefore, shelf life of Group A was determined as 4 months and Group B as 6 months. Throughout the study, the most favorite group is the seabass marinade which was marinated by smoking; in other words, Group B. The differences between two groups was found significant ($p<0.05$).

Thereby, even if parameters of a product quality are acceptable, it is stated as inconsumable when it loses its sensory features [45]. Kaya, stated that the product did not spoil for 200 days but there were only some quality loses in the texture in his plain marinade done by seabass [28]. Balıkçı, stated that there were loses on smell, taste and texture of the products, which were prepared both plain and dilled smoked mackerel marinade, but they were in good quality during 9 months of storing time [29]. Işıdan, examined the quality changes during storing time in 3 different shad marinades (brine, oiled and vacuum packaged). According to his findings, the vacuum packaged product was spoiled on 7^{th} month in sensory perspective; on the other hand, the products which were kept in brine or oil were in better condition on the 7^{th} month [37]. Özoğul et al. stated that sensory features (taste, smell, etc.) of smoked anchovy marinade declined due to storing time, furthermore their shelf lives are 6 months [46]. Even the previous researches resemble to present study, it can be said that shortness of shelf life is resulted from acid-salt rate in the brine and waiting time.

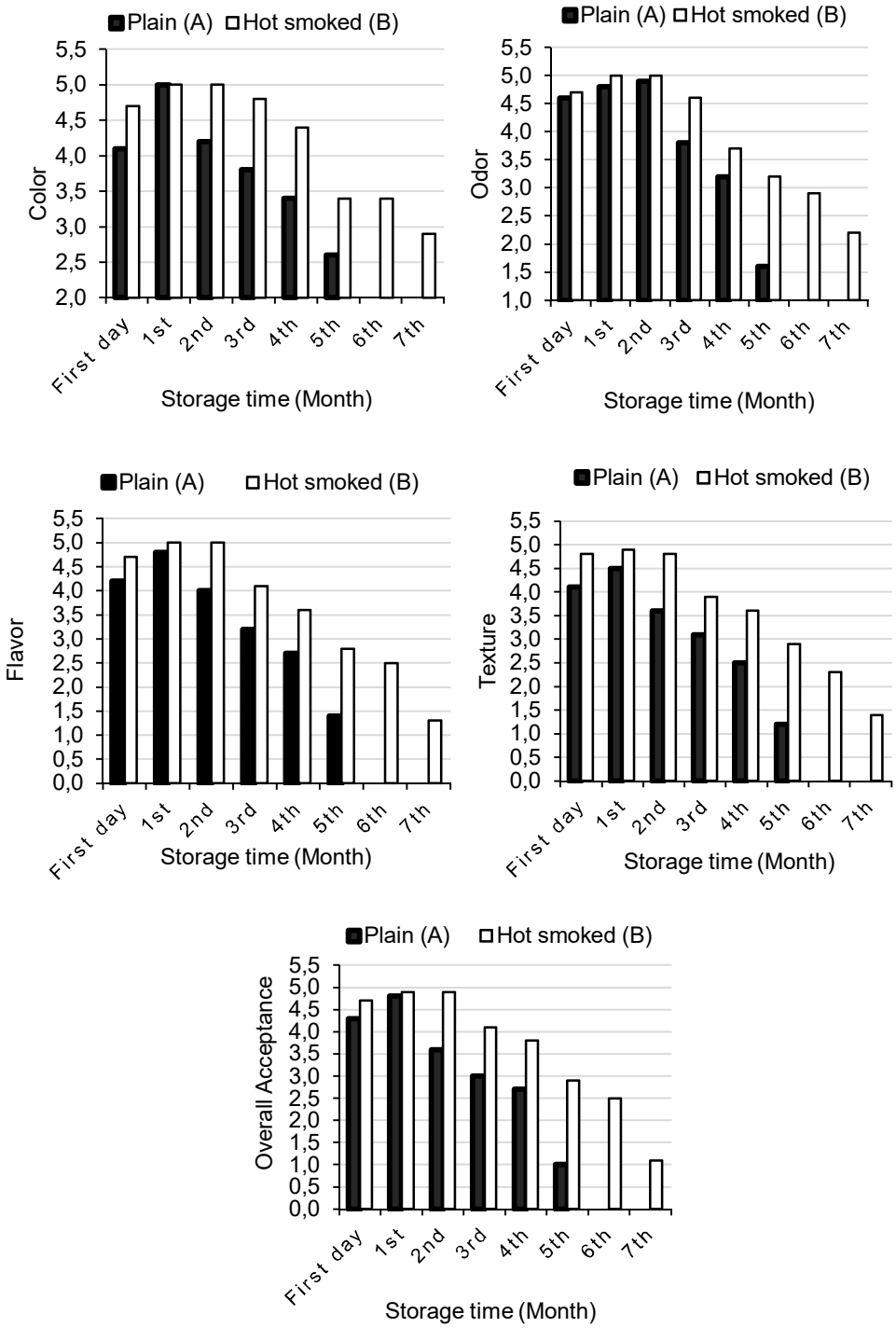

Figure 3. Sensory analyses result of group A and group B

Conclusion

Today, sensory features are at the top when it comes to a product's approval. Even though the product has good quality, when it is not qualified with sensory properties the product is neither preferred nor considered as tradable. It can be said that the results of present study have similar outcomes. Chemical and microbiological values of seabass marinade were between consumable limits; however, since the products have lost their sensory quality, the examination was terminated. According to the findings, shelf life of Group A noted as 4 months, Group B as 6 months. The most favorite group of the study is Group B.

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Using of clinoptilolite, activated charcoal and rock crystal in water purification technology to enhance the biological value of bread kvass

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Abstract

Introduction. It has been determined the influence of drinking running water purified by clinoptilolite, rock crystal and activated charcoal on the vitamin content of wort and kvass.

Materials and methods. The kvass made by kvass rye wort fermentation with the help of yeast Saccharomyces cerevisiae MP-10 was analyzed. The dry matter content was determined by the areometric method, the content of vitamins by the ability of test-cultures to grow in the presence of certain vitamins. Thiamine and riboflavin were determined by fluorometric method.

Results and discussion. In the purified water, the total iron content was 0,01 mg/dm^3, the total water hardness was 1,1 mmol/dm^3, the permanganate oxidation was 0,5 mg O_2/dm^3. The fermentation process was similar to both samples. While the total duration of fermentation of the experimental sample was 13% less, that is due to a decrease in the number of vitamins in the initial wort. The water mineral composition significantly influenced on the content of vitamins in the initial and fermented wort and kvass, in particular, the amount of thiamine and riboflavin in the prototype increased at an average 2.5 times, and the folic acid content at 5 times, that can be explained by the formation in the control sample of water insoluble complexes with bivalent metals. At using model solutions with an index of total water hardness of 5 mmol/dm^3, the thiamine content in the fermented wort decreased by 6,7 times compared to the wort with demineralized water. To ensure high levels of vitamins in the kvass, in particular thiamine, riboflavin and folic acid, process water should have a total hardness no more than 1 mmol/dm^3 and contain no iron ions.

Conclusions. The use of purified water provides the increase in the content of vitamins in the kvass and getting the product with their correlation physiologically acceptable to the human body.

Introduction

Soft drinks are not essential products, but they play an important role in the metabolism of humans [1-4]. Consumption of beverages should not only compensate for the loss of moisture and salts by the body, but also enrich it with vitally necessary biologically active substances, particularly, vitamins [1, 5-7].

When comparing different groups of soft drinks in terms of therapeutic and preventive and general health effects on the human body, fermented beverages are the most promising. Functional fermented beverages based on plant extracts have become significantly more widely used [10-13].

Bread kvass is one of the most popular fermented soft drinks, which is prepared on the basis of rye raw materials by alcohol fermentation [12-14]. In the process of life, yeast ferments carbohydrates with the formation of the main, secondary and by-products of metabolism, as well as vitamins and other biologically active substances [13, 14].

Therefore, the introductions of innovative technologies that increase the biological value of bread kvass, in particular the vitamins content are topical issues of the industry's development.

Water is one of the main components of bread kvass. However, most companies do not carry out additional water treatment as raw materials for kvass production [7, 12].

A promising trend in the food products technology, where water is raw material, is the use of natural minerals, in particular clinoptilolite and rock crystal, as well as active coal at the stage of water treatment [13, 15].

The purpose of the work is to study the influence of clinoptilolite, activated charcoal and rock crystal during the watertreatment stage on the vitamins content in the initial and fermented kvass worts and to determine their correlation according to needs of the human body.

Materials and methods

Purification of water and preparation of model solutions

Treatment of drinking running water was carried out by clinoptilolite of Sokirnitsky field (Ukraine), activated charcoal and rock crystal in laboratory conditions under certain conditions (Patent 116963 Method of water treatment for the kvass production). Clinoptilolite was used to reduce the hardness of water and removal of heavy metals [16, 17]. The structure of clinoptilolite is tetrahedron, the vertices of which form eight-membered rings, inside of which there are water molecules («zeolite water»), and alkaline and alkaline earth metals cations. A large number of input windows on the surface has channels, which provide the use of clinoptilolite as a «molecular sieve» with the replacement of cations (the size of the input windows 3,5–4,8 A°) [18, 19].

Activated charcoal was used to reduce the content of organic impurities and improve the organoleptic parameters of water [13, 20, 21].

Rock crystal was used in order to structure the water, correct the oxidation-reduction potential and remove foreign microflora [6].

In the purified water, the total iron content was 0,01 mg/dm^3, the total water hardness was 1.1 mmol/dm^3, the permanganate oxidation was 0,5 mg O_2/dm^3. For control, untreated water with a total iron content of 0,05 mg/dm^3, a general hardness of 4,5 mmol/dm^3, and a permanganate oxidation of 4,0 mg O_2/dm^3 were used.

For conducting experimental study the optimal parameters of technological water for the kvass production wort was prepared using demineralized water and with a certain amount of hardness salts and iron.

The weight of a model substance was calculated by the formula:

$$m_{рм} = (M_{рм} \cdot C_{мр} \cdot V_{мр})/M_{рр}$$

where $m_{рм}$ is the weight of substance, by means of which the quality of technological water was modeled, mg;

$M_{рм}$ is the molecular weight of the substance used to prepare model solution, g/mol;

$C_{мр}$ is the concentration of model solution, mg/dm^3;

$V_{мр}$ is the volume of the model solution, dm^3;

$M_{рр}$ is the molecular weight of the soluted substance that needs to be modeled, g/mol.

Preparation of kvass wort and kvass

For the cultivation of yeast, the wort was prepared from kvass wort concentrate, sugar syrup and water with the concentration of dry matter 7,0–8,0 %. The wort for preparing kvass was prepared with the concentration of dry matter of 3,4–3,6%, it was fermented with pure yeast culture of Saccharomyces cerevisiae MP-10 (initial concentration of yeast cells in the wort was 0,6 mln/cm^3) at a temperature of 34 °C to reduce the content of dry matter to 0,8–1,0 %. The kvass was prepared by mixing fermented wort separated from the yeast sediment to dry matter content 5,4–5,6 %.

There were prepared two samples of kvass wort:

–control sample is wort on untreated water;

–experimental sample is wort on purified water.

Determination of the vitamins content

The vitamins content was determined by the microbiological method; Thiamine and Riboflavin by fluorometric method; the content of the Thiamine-Catechin complex by the permanganate Leventhal method [16].

As objects of research there were used: drinking water from centralized water supply in Lviv city, activated charcoal Silcarbon, rock crystal, clinoptilolite, kvass wort concentrate, sugar, yeast Saccharomyces cerevisiae MP-10 and finished bread kvass.

Results and discussion

Influence of water purification on the yeast cultivation process and kvass wort fermentation

The biological value of kvass is largely due to the presence of vitamins which are growth factors, and the physiological activity of yeast depends on their amount [3, 4, 13].

The specific growth rate of yeast cells at the yeast cultivation stage is given in Table 1.

Table 1

Specific growth rate of yeast

Duration of cultivation, hours	Specific growth rate, hours^{-1}	
	Control	Experiment
6	0,333	0,464
12	0,368	0,495
18	0,060	0,078
24	0,022	0,028

A higher specific growth rate of yeast on average of 1,3 times throughout the entire cultivating process was observed using the experimental sample of wort.

The dynamics of reducing the dry matters content at fermentation of the experimental and control samples of wort at a temperature of 34 °C is shown in Figure 1.

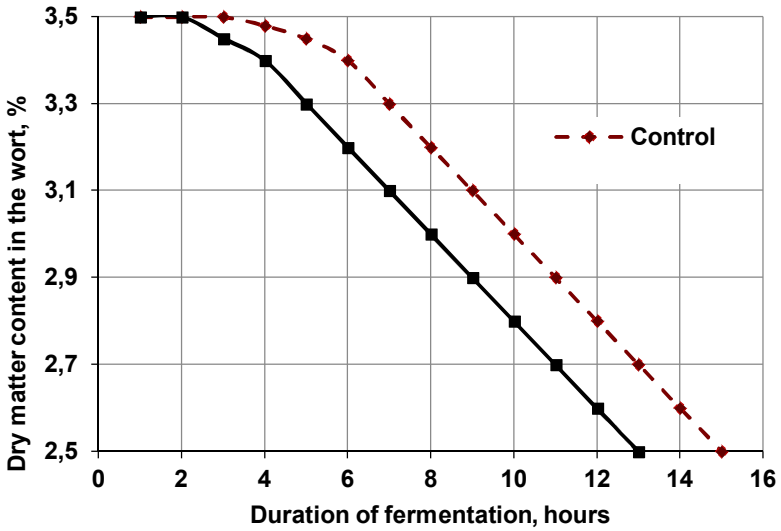

Figure 1. Dynamics of reducing dry matters content at kvass wort fermentation

It was found that the character of fermentation was similar for both samples. However, when using wort on prepared water, the process of intense wort fermentation began already at the second hour, then, for control at the third. In this case, the total fermentation time of the experimental sample was fixed at 13 % less, that is explained by the reduction in the duration of the lag phase of the yeast growth.

The zymase enzymes of yeast are complex substances containing the protein part (apoenzyme) and chemically bound nonprotein (coenzyme). Coenzymes determine the specific activity of the enzyme, take part in its contact with the substrate, and also stabilize apoenzymes. Coenzyme has two functional areas, one of which is responsible for the association with apoenzyme, and the other takes direct part in the catalytic process [22]. It is known that coenzymes contain vitamins which are irreplaceable factors that provide the required rate of biochemical and physiological processes in the yeast cell. The role of vitamins as coenzymes in chemistry of alcohol fermentation is presented in Figure 2 [23].

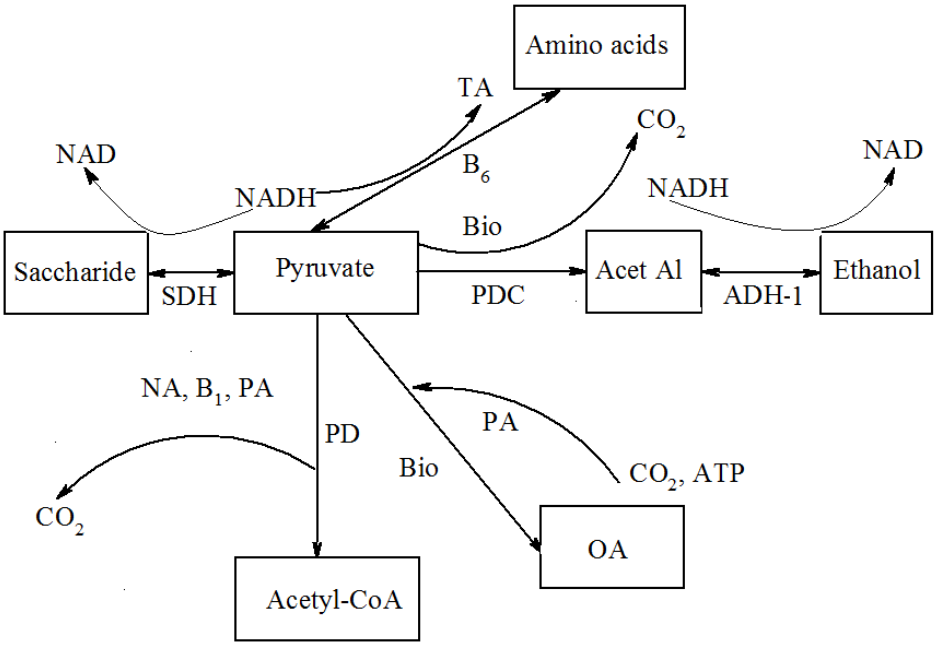

Figure 2. Sugar metabolism in the yeast cell:

PDC – pyruvate decarboxylase;
TA – transaminase;
PC – pyruvate carboxylase;
PD – pyruvate dehydrogenase;
SDH – saccharide dehydrogenase;
ADH-1 – alcohol dehydrogenase;
B_1 – thiamine;
B_6 – pyridoxine;
NA – nicotinic acid;
Bio – biotin;
PA – pantothenic acid;
OA – oxalacetate;
AcetAl – acetaldehyde.

Water influence on the vitamin content of the initial and fermented kvass wort

In determining the vitamin content of the initial wort and fermented wort, the increase in their content after fermentation was determined, this is due to the ability of the yeast to synthesize vitamins [24]. In all samples of fermented wort, the increase in the content of group B vitamins was observed. Table 2 shows the dependence of the vitamin content of the initial and fermented worts on the water used.

Table 2

Content of vitamins in the initial and fermented worts

Vitamins content, μg in 100 g of dry matter	Initial wort		Fermented wort	
	Control	Experiment	Control	Experiment
Thiamin (B_1)	7	16	36	103
Riboflavin (B_2)	5	11	51	122
Niacin (B_5)	480	560	980	1170
Pyridoxine (B_6)	5	12	19	33
Biotin (H)	0,45	0,56	0,76	1,2
Folic acid	2	11	6	28

It was defined that the mineral composition of water significantly influenced the vitamins content in the initial and fermentation wort, in particular the content of thiamine and riboflavin in experimental samples increased at an average of 2,5 times. The highest content was observed for niacin. The increasing vitamin content in the kvass is explainable with their initial raw material content and their creation in the process of yeast life activity.

A significant role in the life activity of yeast cells is played by biotin, which is involved in various metabolic processes, particularly in carboxylation of pyruvate, pyridine nucleotide synthesis, nucleic acids, proteins, polysaccharides, fat acids synthesis, the formation of purine and pyrimidine bases [23, 25]. It is determined the increase in the content of biotin in the fermented wort for experimental and control samples, respectively, at 37 and 20%.

Folic acid is necessary for the formation of new cells and does not have coenzyme properties, but when converted to tetrahydrofolic acid, it participates in DNA replication, amino acid synthesis, in particular methionine and serine, as well as the formation of nucleic acids, pyrimidines and purines. Tetrahydrofolic acid also takes part in the transfer of the methyl, methylene and carbonyl groups, that promotes the activation of enzymes, which take part in fixing the formaldehyde and formic acid residues and their catalytic transformations [23, 25].

The Figure 3 shows the interaction of folic acid with ions of bivalent metals [25].

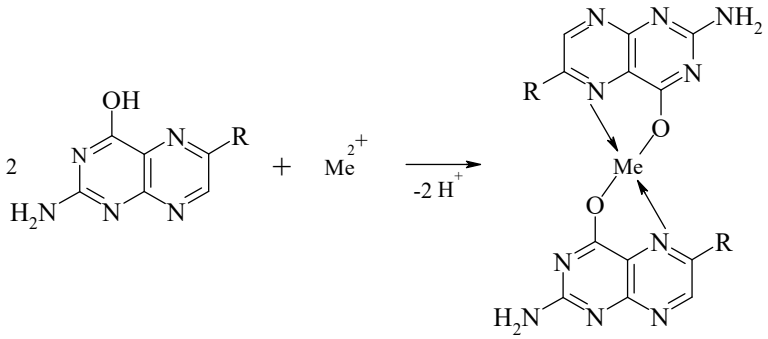

Figure 3. Interaction of folic acid with ions of bivalent metals

In the experimental samples of the initial and fermented worts, an increase in the content of folic acid was observed, respectively, at 5,5 and 4,6 times, that can be explained by the formation in the control of water-insoluble complexes with bivalent metals (Cu^{2+}, Fe^{2+}, Co^{2+}, etc.) by the equation given in Figure 3.

Influence of hardness salts and iron ions on Thiamine and Riboflavin content

One of the most important vitamins for a human body is thiamine, which is formed by condensation of the pyrimidine and thiazole nucleuses [26, 27]. The content of thiamine in drinks substantially depends on the calcium and magnesium salts, which reduce its solubility. Therefore, reducing the hardness of technological water allows increase the amount of thiamine, and therefore increase the biological value of kvass. In addition, thiamine positively effects the process of fermentation of the wort, increasing its speed. Coenzyme thiamine diphosphate is used by yeast in the reactions of the conversion of pyruvic acid to acetaldehyde, which is a determining factor in alcohol fermentation [28]. Thiamine also regulates the condensation of acetone and the formation of butanediol-2,3, that effects the taste and aroma properties of kvass [29].

Riboflavin is not the factor in the growth of yeast, but it participates in oxidative-reduction reactions under anaerobic conditions [23, 25]. Yeast synthesizes this vitamin in significant quantities. At the same time, its content in kvass depends on the concentration of iron ions, which move into wort both with concentrate kvass wort (CKW) and with water.

The influence of hardness salts and iron ions on Thiamine and Riboflavin contents in fermented wort is shown in Figure 4 and 5.

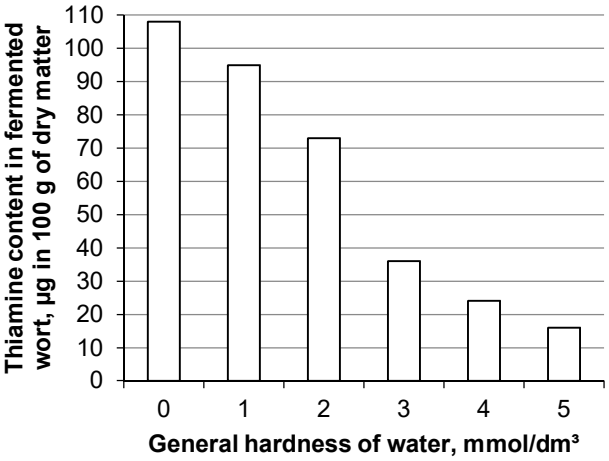

Figure 4. Influence of hardness salts on Thiamine content in fermented wort

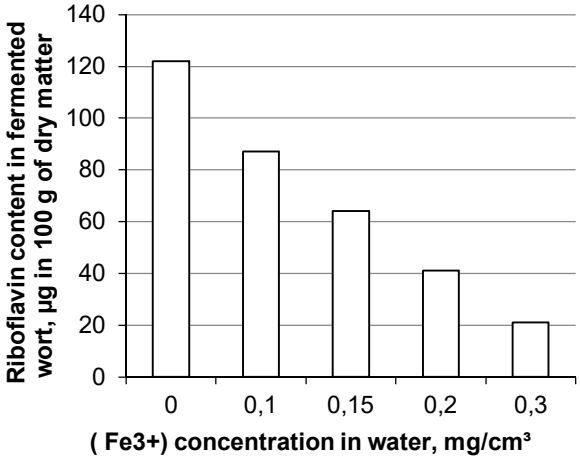

Figure 5. Influence of Fe^{3+} ions on Riboflavin content in the fermented wort

It was defined that when using model solutions with the index of general hardness at 5 mmol/dm^3, the Thiamine content in the fermented wort decreased by 6,7 times compared with the wort in demineralized water. The water hardness of 1 mmol/dm^3 the Thiamine content decreased only at 12 %, that is explained by the interaction of Thiamine with calcium and magnesium salts.

It was established that with increasing concentration of iron ions in water up to 0,3 mg/cm^3, the content of riboflavin in the fermented wort decreased 6 times.

These data observe Calcium, Magnesium and Ferrum ions have the significant influence on the Thiamine and Riboflavin content in the fermented wort. While it is probable, insoluble in water complexes with iron ions are formed.

Thus it has been established that in order to ensure high content of vitamins in kvass, particularly Thiamine, Riboflavin and Folic acid, technological water should have total hardness of no more than 1 mmol/dm^3 and should not contain iron ions.

Assessment of the biological value of kvass

In order to estimate the biological value of kvass in accordance with the requirements of FAO/WHO, an average daily maintenance of vitamins at a consumption of 0,5 dm^3 of beverages has been calculated. Profiles of the vitamins content of the control and experimental samples of kvass are shown in Figure 6.

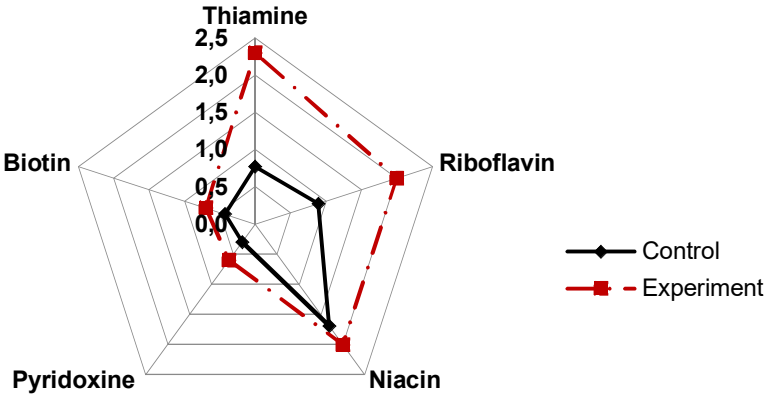

Figure 6. Profile of daily maintenance of vitamins at consumption of 0.5 dm^3 kvass

It was defined that when using kvass 0,5 dm^3, the daily requirement for vitamins of group B and niacin is provided by 0,5–2,4 %, which is acceptable, since soft drinks are not the main component of vitamins in the human body. From the investigated vitamins, the most consistent with the daily needs are thiamine, riboflavin and niacin. With the use of prepared water the provision human body with these vitamins increases at an average of 2 times (respectively 3, 2,5 and 1,6 times). This can be explained by their taking part in biosynthetic processes of yeast cells.

As you know, a human ration should contain a variety of foods. In this case, the main thing is not the quantitative content of biologically active substances, but their adequacy in accordance with the needs of the human body [26, 27]. The ratio of vitamins in the control and experimental samples in accordance with the physiological needs of the human body is given in Table 3; where for 1 standard unit the established requirements of the daily requirement of vitamins are adopted, and the value of experiment and control is the ratio of their respective content in beverages to the norm. Proximity to 1 standard unit indicates that the content of this vitamin is more in line with FAO/WHO requirements.

Table 3

Ratio daily providing with vitamins

Name	The ratio of vitamins, standard unit				
	Thiamine	**Riboflavin**	**Niacin**	**Pyridoxine**	**Biotin**
Control	0,155	0,179	0,343	0,059	0,001
Experiment	0,444	0,427	0,410	0,103	0,002

It was found that the experimental sample compared to control ones most meets determined requirements for Thiamine, Riboflavin, Niacin, Pyridoxine and Biotin, respectively, 2,9; 2,4; 1,2; 1,8; 2.0 times**.**

So, kvass is prepared using the purified water by the proposed method and has the increased biological value.

Conclusion

It has been established that the use of clinoptilolite, rock crystal and activated charcoal during water purification in bread kvass technology provides an increase in the content of vitamins in the initial and fermented wort and the getting of the finished product with the physiological needs acceptable for the human body with the ratio of thiamine, riboflavin, niacin, pyridoxine and biotin.

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Determination of the parameters of the recovery systems of heat potentials of streams of the gas-steam media

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Abstract

Introduction. The paper concerns the determination of the relations of energy potentials in mass flows of gas and steam-gas systems and their changes in thermodynamic transformations and regeneration possibilities.

Materials and methods. Researches are presented in the form of phenomenological generalizations on the basis of the laws of chemistry, thermodynamics with thermochemical calculations based on Hess's law.

Results and discussion. Transformation of incoming gas streams used as the primary sources of chemical energy potentials with conversion into thermal energy is accompanied by losses at the level of heat of condensation of the formed vapor phase. Vapor-gas mixtures are generated in the processes of drying, aeration of grains for germination, in systems of aerobic fermentation processes, in the aeration of industrial wastewater, etc.

The course of such processes takes place in thermodynamic parameters, which do not correspond to similar characteristics of the environment, which is accompanied by energy losses at the levels of difference between their enthalpies. From this point of view, an important component of such gas-steam mixtures is the steam fraction of water, since it carries the thermal potential of vaporization.

The article discusses the ratio of parameters of material and heat flows, provides information that the energy potential of condensation of the vapor phase in products of combustion of gases is close to 10% of their calorific value.

The estimation of the prospects of the application of heat pipes in heat recovery systems by the creation of closed energy circuits is evaluated. It is shown the possibility of combining heat exchanging surfaces of cooling and heating with heat pipes, which achieve the same parameters of the temperature of evaporation and condensation of intermediate thermal agents, the thermodynamic parameters of the latter in terms of the possibility of their application in the systems being created are given.

With the presence of energy converters in the form of compressors and gas-expansion machines, the recovery systems are converted into local heat pumps.

The use of methane, ethane, propane and butane as the primary source in the formation of water vapor is carried out in quantities corresponding to their chemical formula, depending on the ratio of the number of atoms of carbon and hydrogen. Recuperative recovery of the energy of the output vapor-gas mixture is expedient to carry out in the direction of the input air flow in systems with an intermediate coolant and implementation of heat exchange processes with the simulation of effects of thermal pipes or with the addition to the schemes of heat pumps.

Conclusions. The schemes of thermodynamic processes confirm the possibilities of applying the proposed thermodynamic transformations.

Introduction

Energy flows and their transformations in the processes of food technologies are, in most cases, associated with material flows that are carriers of the first [1]. At the same time, energy potentials in the form of the chemical energy of input flows of raw materials, semi-products and finished products are the subject of the main interests of any technology [2]. Chemical and biochemical reactions associated with the transformation of material flows are accompanied by the release or absorption of energy [3]. More often, such energy is represented by heat and the magnitudes of thermal effects in thermochemical equations are represented by a "plus" sign in exothermic reactions and a "minus" sign for endothermic interactions [4].

In a significant number of technologies in food industries biochemical transformations of material flows in the directions of both resynthesis and synthesis of more complex substances are used. Forms of energy contained in different substances and released during chemical reactions or in the course of physical processes (for example, during condensation of steam or liquid crystallization), are defined as the internal energy of substance [5].

The thermal effects of such reactions depend on the nature of the inputs and reaction products, their aggregate state and temperature. The latter often values their energy potential, which deserves the full recovery and use at the levels of technologies of heat pumps [6, 7].

Modern studies are aimed at the prospects of using secondary low-potential heat resources [8], the creation of high-temperature heat pumps [9], the use of heat pipes in geothermal heat pump systems [10], the creation of combinations of heat pumps with solar energy utilization systems [11] and absorption-compression pumps [12]. The urgency of addressing the problems of the recuperation of secondary energy recourses is due to the fact that the industrial sector consumes one-third of the world energy with subsequent its transformation into thermal energy at the level of 50% [7].

The purpose of the study was to determine the energy potential of the media formed as a result of the transformations of material flows with the formation of gas-steam mixtures and the prospects for their use.

Materials and methods

Research are presented in the form of analytical and phenomenological generalizations, based on the laws of chemistry and thermodynamics. Thermochemical calculations are performed on the basis of Hess's law, which determines that the thermal effects of the reactions depend only on the initial and final states of matter [13].

The used provisions are related to the laws of conservation and transformation of the mechanical and internal energy of systems, taking into account the equations of ideal and real gases, the first and second laws of thermodynamics, information about the thermodynamic parameters of refrigerant agents and the laws concerning energy and entropy balances.

Results and discussion

In modern conditions, the role of energy primary sources is often performed by representatives of a homologous series such as methane, ethane, propane and butane, the combustion of which leads to the formation of carbon dioxide and water in accordance with the reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O; \qquad 2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O;$$
$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O; \qquad 2C_4H_{10} + 13O_2 = 8CO_2 + 10H_2O. \quad (1)$$

Let's turn to calculations of thermal effects. It is known that the heat of formation of "liquid" water is 285.8 kJ/mol [14]. This means that the synthesis of 18 g of water from 2 g of hydrogen and 16 g of oxygen is accompanied by the release of 285.8 kJ of thermal energy. However, the heat of formation of water steam equals 241.8 kJ/mol, which corresponds to the thermochemical equation:

$$H_2O_2 + \frac{1}{2}O_2 = H_2O_{(s)} + 241.8 \text{ kJ}. \quad (2)$$

It is obvious that the difference of 285.8 – 241.8 = 44 kJ is attributed to one mole (18 g) with the heat of evaporation of water at 25 °C.

The equation corresponds to the formation of carbon dioxide

$$C + O_2 = CO_2 + 393.5 \text{ Kj}.$$

The thermal effect of the methane oxidation reaction CH_4 for the known heat of its formation (74.9 kJ/mol) and its products of combustion – carbon dioxide (393.5 kJ/mol) and water (285.8 kJ/mol) is equal to

$$CH_4 + 2O_2 = CO_2 + 2H_2O + (-74.9 + 393.5 + 571.6) = 890.2 \text{ kJ}, \quad (3)$$

which corresponds to Hess's law [15].

The ratio of the composition of hydrogen and carbon follows from the formula C_nH_{2n+2} where n is the number of carbon atoms comes out from the homologous series of saturated hydrocarbons.

Thus, the combustion of natural gases is accompanied by the formation of a mixture of CO_2 and H_2O in the form of the steam fraction of the latter, since its temperature is greater than 100 °C with energy losses at its thermal capacity. An important component in the latter is the proportion of the heat of steam formation of water, which can be turned to technological needs by condensation of water steam [16].

The dependencies (1)–(3) give the material relations on the basis of which the calculations on the quantities of the generated steam and heat of its condensation are made (Table 1).

Table 1

Ratio of material and energy indicators

System parameter	Gas			
	Methane CH_4	**Ethan C_2H_6**	**Propane C_3H_8**	**Butane C_4H_{10}**
Molecular weight	16	30	44	58
The ratio of the N / C atoms	4	3	2.67	2.5
Number of H_2O at burning of 1 kg of gas, kg	2.25	1.8	1.636	1.552
Heat of condensation of H_2O, kJ	5081.4	4065.14	3694.8	3505

Obviously, the expediency of recuperative return of heat of condensation can be determined in comparison with the calorific value of gases. According to the known value of the theoretical indicator of this value for methane 890.2 kJ/mol, the conversion to 1 kg of its mass gives a value of 55108 kJ. However, according to reference data, it is 49.800 kJ/kg, for propane it is 46.400 and for ethan it is 47.500 kJ/kg. This means that the indicator of the recuperative effect is approaching to 10% of the total indicator of calorific value [14].

Products of combustion of gases in the form of a mixture of CO_2 and H_2O as material flows simultaneously serve as energy streams. The efficiency of the use of the latter depends on the organization of heat transfer to other material flows and the thermodynamic parameters of such processes.

From the point of view of the interests of the stability of the recuperative regimes of the return of heat of condensation it is expedient to consider the use of the heater of the income air flow. In this case, it is important the incoming air streams and outcome mixtures to be maximally synchronized.

In the classical schemes of installation of steam generators, the spent steam-gas mixture gives its energy potential for the heating of nutritious water in the economizer and in the air heater. However, for example, there are no economisers in the dryers for malt, and the installation of an air heater, in which there is a heat transfer between two significant streams of air gas-steam mixture, has noticeable complexity. The latter are related to the achievement of the calculated surface of the heat transfer and the limited temperature difference as driving factors. The use of the idea of a heat pipe corresponds to such option, which is accompanied by the presence in the system of an intermediate coolant with thermodynamic parameters in the regimes of phase transitions [17]. The achievement of these regimes in the evaporator and condenser depends on the thermodynamic characteristics of the intermediate coolants. In the tables 2 and 3 there are given the following characteristics for some substances that may be used in their role.

It follows from the data that the relationship between the pressures and temperatures of the refrigerants could satisfy the modes of phase transitions in the evaporator, but such upper limit as 50 °C limits the condensation temperature. However, in a system that is an analogue of a heat pipe, the phase transitions in the evaporator and the condenser should be carried out with minimal difference of temperature.

This analysis leads to the conclusion that the search for other substances for the role of the intermediate coolant is incomplete, and the achievement of satisfactory values of temperature variations is possible only with intervention to the thermodynamic cycle.

Table 2

Thermodynamic parameters of refrigerating agents

Indicators	Ammonia	Butane	Carbon dioxide	Ethan	Chlorine ethyl	Izobutan	Propane
Chemical formula	NH_3	C_4H_{10}	CO_2	C_2H_6	C_2H_5CCl	$(CH)_3CH$	C_3H_8
Molecular weight	17.032	58.1	44.005	30.058	64.51	58.1	44.079
Volume mass of liquid, kg/l	0.6818	0.6	Non-liquid at 0.1 MPa	0.5459	0.9232	0.6	0.5853
Boiling temperature at 0.1 MPa, °C	– 33.35	0.6	–	– 88.3	13.1	– 13.3	– 44.5
Critical temperature, °C	132.9	150.8	31.0	32.1	182.8	133.7	95.6
Heat of steam generation at 0 °C, kJ/kg	1257.8	388.4	231.3	328.5	401.4	388.4	376.7
Value of heat capacities c_p/c_v	1.297	1.108	1.3003	1.224	1.1257	1.11	1.153
Suction pressure at –10 °C, MPa	0.793	0.0738	2.71	1.88	0.0411	0.15	0.359
Condensation pressure at 30 °C, MPa	1.18	0.302	0.73	0.477	0.1905	0.46	1.119
The pressure ratio at +30 °C in the condenser and at –10 °C in the evaporator	4.03	4.09	2.7	2.54	4.63	4.0	3.11

Table 3

Parameters of a saturated steam of refrigerators

Absolute pressure, MPa	t, °C	Specific volume		Specific enthalpy		Specific entropy	
		liquid V′, l/kg	steam V″, m^3/kg	liquid i′, kJ/kg	steam i″, kJ/kg	liquid S′, kJ/(kg·K)	steam S″, kJ/(kg·K)
Ammonia							
2.03	50	1.78	0.064	659	1712	4.99	8.25
1.56	40	1.73	0.083	609	1711	4.83	8.35
1.17	30	1.68	0.114	555	1706	4.66	8.47
0.85	20	1.64	0.149	512	1700	4.52	8.57
0.62	10	1.6	0.206	465	1692	4.35	8.69
0.43	0.0	1.57	0.290	419	1682	4.19	8.81
0.29	– 10	1.53	0.419	372	1671	4.02	8.95
0.19	– 20	1.5	0.620	327	1657	3.84	9.10
0.12	– 30	1.48	0.960	282	1642	3.66	9.26
0.072	– 40	1.45	1.550	237	1626	3.47	9.44
0.041	– 50	1.42	2.630	193	1610	3.28	9.63
Chladon-12							
1.21	50	0.83	0.014	449	572	4.16	4.54
0.96	40	0.80	0.018	439	568	4.13	4.55
0.74	30	0.77	0.024	429	565	4.10	4.55
0.57	20	0.75	0.031	419	561	4.07	4.55
0.42	10	0.73	0.014	410	556	4.03	4.55
0.309	0.0	0.72	0.056	400	552	4.00	4.56
0.22	– 10	0.70	0.077	391	548	3.97	4.56
0.151	– 20	0.69	0.109	381	543	3.93	4.57
0.101	– 30	0.67	0.160	372	538	3.89	4.58
0.064	– 40	0.66	0.242	363	534	3.86	4.59
0.039	– 50	0.65	0.383	355	529	3.82	4.60

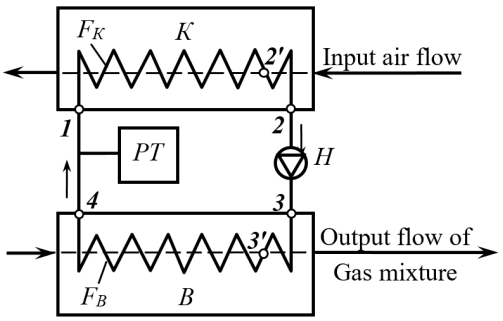

Figure 1. Scheme of the contour of the intermediate coolant:
B – evaporator; K – capacitor; RT – pressure regulator; H – pump; FK – heat transfer surface of condenser; FV – surface of the heat transfer of the evaporator

In Figure 1 it is a schematic diagram of the internal coolant for contour system in which the return of the condensate can be achieved at the expense of gravitational forces or forced by the use of the pump (Patent of Ukraine 14523). For identical pressures on the heat transfer surfaces of the condenser and evaporator, the temperature of the steam phase in them will be the same.

Depending on the intensity of the heat transfer processes in the condenser, the condensate may leave it at a temperature of the steam phase or lower. The processes shown in Figure 2 in coordinates of T-s correspond to these two cases. To intensify the heat exchange, it is expedient to limit the area of condensate overcooling.

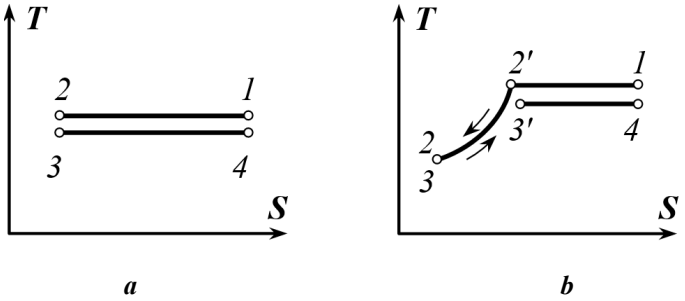

Figure 2. Diagrams of processes:
a - without re-cooling of the condensate:
1-2 – condensation of steam; 3-4 – formation of the steam phase in the evaporator;
b - with supercooling and post-heating of condensate:
1-2' – condensation of steam; 2'-2 – overcooling of the condensate;
3-3' – post-heating of condensate; 3-4 – formation of the steam phase in the evaporator

Further improvement of systems is connected with the forced transformation of steam of intermediate coolant due to changes in pressures in the system. For this, the contour is supplemented by a compressor and a regulator valve or a gas-expansion machine on the return section (Figure 3).

Case in the Figure 3 refers to the use of a steam-liquid intermediate coolant, and a scheme in the Figure 3, *b* refers to gas intermediate coolant.

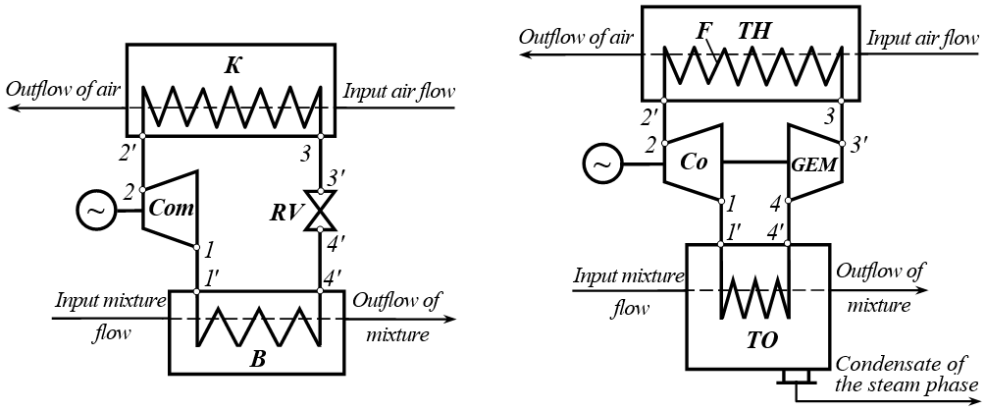

Figure 3. Schemes of devices with transformers of thermodynamic parameters of the steam phase: a - with compressor Com and regulator valve RV;
b - with compressor Com and gas-expansion machine GEM

The presence of an intermediate compression of the steam or gas phase means an increase

in their temperature. Due to the limited time of the processes of compression, they will be considered to be adiabatic as well as processes of throttling of condensate in the regulator valve and in gas-expansion machine.

Addition of the scheme in Figure 3 a, with compressor and regulator valve transforms the device into a device with characteristics of a heat pump. The processes occurring in it are reflected in Figure 4 in coordinates T-s.

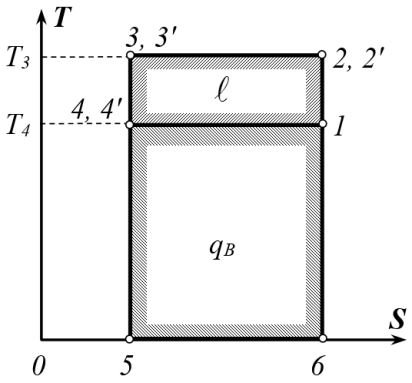

Figure 4. Scheme of the thermodynamic cycle in the coordinates T-s:
1-2 – adiabatic compression of the steam phase;
2'-3 – condensation of the steam;
3'-4 – throttle of condensate; 4'-1' – formation of the steam phase

The compression of the steam of the intermediate coolant means that condensation and formation of the steam phase occur at different pressures and temperatures. Obviously, this creates conditions for increasing the temperature of the ouflow from the condenser in favor of increasing the overall efficiency of the system. The areas in the diagram (Figure 4) reflect the energy contribution of various components.

The area 1-4-5-6-1 reflects the amount of thermal energy selected from the outflow of the gas-steam mixture, the area 1-2-3-4-1 represents the amount of energy introduced into the system by the compressor.

The thermal energy transmitted to the input air stream is shown in the diagram with an area of 1-2-3-4-5-6-1. It is obvious that the proportion of thermal energy, which is selected from the outflow of the gas mixture, must essentially exceed the proportion of energy introduced into the system from the compressor.

As in the case of reflection of the analytical relations of theoretical cycles of heat pumps, in the study of this scheme, there are dependencies

$$q_c = q_e + \ell \text{ , kJ/kg,} \tag{4}$$

where q_c i q_e – specific heat load per unit mass of the coolant in the condenser and evaporator respectively; ℓ – specific energy introduced into the system by a compressor.

The work of adiabatic compression of ateam of the intermediate coolant in specific calculation is determined by the dependence:

$$\ell = \frac{R}{k-1}\left(T_2 - T_1\right), \text{ kJ/kg,} \tag{5}$$

where R – universal gas constant, J/(kg·K); k – adiabatic indicator.

To determine total energy consumption, it is necessary to find the magnitude of the flow of the intermediate coolant circulating in the circuit.

At the known temperature of the input air flow at the entrance to the heater t_{in1} and at the output of it t_{in2}, the power of the required energy flow should be

$$Q_{con} = c_a m_{air} \left(t_{in1} - t_{in2} \right), \text{ kW}, \tag{6}$$

where c_a – the heat capacity of air, adopted as the constant value, kJ/(kg·K); m_{air} – mass flow of air, kg/s.

Herewith

$$Q_{con} = Q_{ev} + L, \text{ kW}, \tag{7}$$

where Q_{ev} – the power of the heat flow from the evaporator, kW; L – power of the heat flow introduced by the compressor, kW.

Hence the theoretical load on the evaporator

$$Q_{ev} = Q_{con} - L, \text{ kW}. \tag{8}$$

The energy flux of the evaporator is transferred by the intermediate coolant in the state of the steam phase, and therefore its mass flow is determined by the condition

$$m_{i.c} = \frac{Q_{ev}}{r} = \frac{Q_{con} - L}{r}, \text{ kg/s}, \tag{9}$$

where r – specific heat of vaporization of intermediate coolant.

To estimate the relations of mass flows, we will make corresponding calculations.

Although earlier it was noted that the heat capacity of the air is assumed to be constant, we still give data relating to this value in the range of temperatures from 0 to 500 °C:

Temperature, °C	**Mass heat capacity of air, kJ/(kg·K)**
0	1.0036
100	1.0061
200	1.0115
300	1.0191
400	1.0283
500	1.0387

Declining values c_{pm} in the specified range is about 3.5 % and evaluating the temperature values as $t_{in1} = 0$ та $t_{in2} = 200\,°C$, we accept c_{pm} = 1.006 kJ/(kg·K). Then specific costs are calculated on a mass flow m_{air} = 1 kg/s will be

$$Q_{con} = 1.006 \cdot 1{,}0 \cdot 200 = 201.2 \text{ kW}.$$

Let's assume that the energy contribution of the compressor is 10 % from Q_{con}. Then

$$Q_{ev} = 201.2 - 20.12 = 181.08 \text{ kW}.$$

The specific heat of vaporization of an intermediate coolant will be taken at a level of 2200 kJ/kg and then its mass flow will be

$$m_{i.c} = \frac{181.08}{2200} = 0.082 \text{ , kg/s.}$$

To calculate the volumetric flows of the steam phase of the intermediate coolant, we turn to the corresponding ratios at different pressures related to the saturated steam:

Pressure of steam, MPa	**Specific volume of steam v″, m³/kg**
0.101	1.673
0.19854	0.8917
0.313	0.582
0.4155	0.4461
0.476	0.3926

For the obtained data and at $m_{i.c} = 0.082$, kg/s volumetric flows are determined by the dependence

$$v'_{i.c} = m_{i.c} v'' , \tag{10}$$

where v″ – specific volume of steam, m³/kg.

According to these pressures they will br 0.1372; 0.0731; 0.0477; 0.0366; 0.0322 m³/s.

Accepting the velocity of the steam phase of the intermediate coolant w = 50 m/s, we determine the geometric parameters of the cross-section of the pipelines:

$$f = \frac{v'_{i.c}}{w}; \qquad d = \sqrt{\frac{4v'_{i.c}}{\pi w}} , \tag{11}$$

where f – the cross-section of the pipeline; d – pipeline diameter.

For a number of obtained values $v'_{i.c}$ we get the appropriate number of diameters:

d = 0.059; 0.043; 0.0349; 0.0305; 0.0286 m.

For the possibility of using machine calculations, we give a generalized formula for determining the diameter d:

$$d = 2\sqrt{\frac{0.9 c_a m_{air} \left(t_{in1} - t_{in2}\right)}{\pi r} \cdot \frac{v''}{w}} = 1.0707\sqrt{\frac{c_a m_{air} \left(t_{in1} - t_{in2}\right)}{r} \cdot \frac{v''}{w}} . \tag{12}$$

From the obtained values of the diameters, it is possible to conclude that in terms of constructive solutions, they are quite acceptable. Similar results are quite expected taking into account the high levels of heat flows transmitted by heat pipes. The reduction of elements into the system, which transform it into a heat pump, means that it can be used in the

conditions of the limited values of the output flow temperatures.

The latter may be suitable for dryers in which the initial material flows are doubled.

One of these outflows is a gas-steam mixture produced by the combustion of the primary energy carrier, and another is an exhaust-drying agent, which is formed by heating the air flow by its interaction with the medium. In the latter case, depending on the design solution and technological regimes at the relatively high temperature potentials of the isoenthalipic processes of drying temperature characteristics can be limited. Such ratios make it possible to estimate such flows as low-potential ones.

Scheme in Fig 3, b concerns the case when gas circulating in a circuit without phase transitions acts as an intermediatecoolant. Under these conditions, the driving factor of heat transfer in the heat exchanger-heater HEH and the heat exchanger-cooler HEC increases due to diabatic compression of gas in the compressor and additional cooling by adiabatic expansion in gas-expansion machine, respectively.

The presence of a sealed cooling surface in the heat exchanger HEC means the possibility of condensation of the steam phase from a mixture of gases in favor of increasing the level of recovery energy return into the inflow of air.

The heat transfer in the heat exchanger HEH in the direction from the intermediate heat carrier to the input air stream is accompanied by a decrease in the temperature of the first in the direction from point 2 to point 3. Depending on the construction of the transport elements of the heat transfer surface F, the pressure in it can be stabilized or will decrease.

If in the preceding case (Figure 4) isotherms 2-3 and 4-1 are simultaneously isobars, then according to the scheme in Figure 3, b such coincidence is not obligatory. The diagram of the thermodynamic cycle for this case is shown in Figure 5 and 6.

The area 4-1-6-5-4 reflects the amount of heat perceived in the HEC, the area 1-2-3-4 is the amount of energy introduced into the stream by the compressor, and transferred to the air flow in HEH thermal energy, equivalent to the area of 1- 2-3-4-5-6-1.

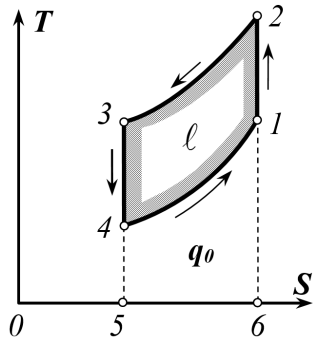

Figure 5. Scheme of the thermodynamic cycle in the coordinates T-s for the case in the scheme of Figure 3, b:

1-2 – adiabatic compression of the intermediate heat-carrier in the compressor;
2-3 – polytropic cooling;
3-4 – adiabatic expansion in gas-expansion machine;
4-1 – polytropic heating in the HEC

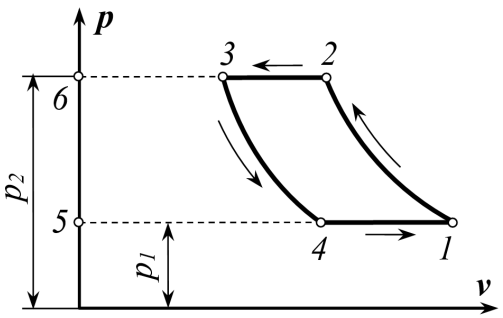

Figure 6. Scheme of the thermodynamic cycle in the coordinate's p-v for the case in the scheme of Figure 3, b:

1-2 – adiabatic compression of an intermediate coolant in a compressor;
2-3 – isobaric cooling;
3-4 – adiabatic expansion in gas-expansion machine;
4-1' – isobaric heating of the intermediate coolant in the HEC

For the isobaric processes heat transfer processes in the heat exchangers HEH and HEC the diagram of the thermodynamic cycle in the coordinates p-v is shown in Figure 6.

The area 1-2-3-6-5-4-1 in this diagram shows the compression energy of the compressor, and the area 3-6-5-4-3 – the work received in gas-expansion machine. The amount of thermal energy subtracted from the output stream:

$$q_0 = c_{pm}\left(T_1 - T_4\right), \tag{13}$$

where c_{pm} – average mass heat capacity at constant pressure.
The energy entering to the cycle by the compressor,

$$\ell = c_{pm}\left(T_2 - T_1\right). \tag{14}$$

The energy returned by the gas-expansion machine to compressor,

$$\ell_{gem} = c_{pm}\left(T_3 - T_4\right). \tag{15}$$

The mass flow of the intermediate coolant is

$$m_{i.c} = \left(Q_{TH} - L\right)/q_0, \tag{16}$$

where Q_{TH} – the power of the heat flow, transmitted to the inlet air flow in HEH; L – power of the power flow of the gas-expansion machine.

The disadvantage of the system with gas intermediate coolant is the relatively low heat capacity of the gas.

Conclusions

The performed researches allow to note the following.

1. The use of such representatives of the homologous series as methane, ethane, butane and propane as energy primary sources leads to the formation of water steam in quantities corresponding to their chemical formulas, depending on the ratio of the numbers of carbon and hydrogen atoms in the compounds.
   With the decrease of the molecular mass of gases for identical mass flows, taking part in energy transformations, the amount of water steam increases.
2. A mixture of carbon dioxide and water steam in products of combustion is characterized by the energy potential of condensation of the latter at levels of about 10% of the calorific value of gases. Hence the expediency of creating systems for the recovery return of the thermal potential of the steam phase.
3. The achievement of modes of condensation of water steam and the separation of condensate from the steam-gas mixture means the need to cool the latter to temperatures below 100 ° C for the implementation of this process at pressures close to atmospheric. This means that such a heat transfer simultaneously will allow to make deep utilization of the thermal energy of carbon dioxide as a component of the mixture.
4. Recuperative return of energy of the output steam-gas mixture should be carried out in the direction of the input air flow in systems with an intermediate coolant and the implementation of heat transfer processes simulating the effects of the heat pipe or with the addition of the schemes of heat pumps. The analysis of the thermodynamic cycles of the latter indicates that water can be used as an intermediate thermal agent that operates in phase transition modes.

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Modeling of heat transfer deterioration regimes when concentrating solutions in industrial film evaporators

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Abstract

Introduction. Heat transfer deterioration in film evaporators may occur without breaking the integrity of film is termed as boiling crises of the 2-type (dry out). The mechanism and mathematical model of heat transfer at ultrahigh concentrations are developed.

Materials and methods. Physical modeling of the thermal-hydrodynamic characteristics of the annular down flowing vapor-liquid streams of highly concentrated sugar solutions is carried out in an experimental set up with a pipe of 9 m long, 30 mm diameter, divided into 20 sections for discrete measurements of the heat flow, fluid concentration and film temperature of the pipe wall.

Results and Discussions. The mathematical modeling of heat transfer in flowing films of dense sugar solutions is based on the equations of convection and thermal conductivity with a parabolic velocity profile in the film. The model, shows that the correspondence with the experimental data on heat flux decrease along the evaporation channel occurs due to the periodic film mixing by the large waves (inflows). The mode of heat transfer deterioration is ascribed to the interaction of cyclical processes of increasing concentration on the interphase surface with the correspondent increase in temperature depression. Analytical expressions for calculating the increased interphase concentrations and decrease of the heat flux are provided within the wave cycles. The reduction of the wall heat flux along the entire channel is accounted for by means of zonal calculations with a step corresponding to the length of the large waves. Experiments do not show an abrupt decrease of heat flux along the pipe, but the reduction of HTC at concentrations of 75% and higher. The Prandtl numbers varied within the values of 25–350 along the evaporative pipe, accompanying the decrease in heat flux. The recommended correlations are valid within the heat flux variation of 3–15 kW/m^2, wetting flow rate 0,05–0,3 kg/m s. Maximum deviation of the HTC calculated values from those observed in practice not more 15%.

Conclusions. The developed model, depicting the process of heat transfer in film with a super-high concentration of liquids, adequately reflects the processes of heat transfer deterioration to dense films in long channels.

Introduction

A number of research projects of the heat transfer to the falling liquid films point out that there might happen a critical deterioration of heat transfer which is attributed to the disruption of the liquid film integrity. This usually occurs as a result of film thinning due to the evaporation and respective reduction of liquid flow rate in the film or it may also be accompanied by the liquid droplets entrainment by the co-current steam flow [1]. Another mechanism of heat transfer deterioration which is caused by the non-linear interaction of gravity – capillary waves and oscillating thermocapillary instability has been addressed in [2]. This effect (called effect Marangoni), when applied to the liquid film flows, cases disruption of the film integrity and appearing of a system of rivulets, which in turn, causes a significant decrease in heat transfer along with the local overheating of heat transfer surface.

The mechanism of the film's integrity disruption due to the local film dry out is addressed in [2, 3] and the disintegration of films as a result of the Marangoni effect – in [4, 6]. In case of the significant increase in the concentration of evaporated solutions in the regimes of down flows in the industrial film evaporators, a noticeable growth of the concentrated solution's viscosity takes place. This leads to the lowering of the film's speed along with the respective increase of its thickness. This factor might be preventing in the disruption of the liquid film. Thus, when analyzing the process of a solution concentration, one may mark two competing effects: the first is – film's thinning down along the evaporative surface due to the evaporation of liquid, which leads to the film disruption; the other one – gradual increase of liquid's viscosity due to the solvent evaporation, which cases film thickening and thus, prevents loss of its integrity. In the event of the thick highly concentrated solutions evaporation, the rate of liquid viscosity growth prevails over the decrease in the flow rate due to the evaporation. Therefore in the above conditions, the mean film thickness will definitely grow up, in contrast to the similar processes of water films evaporation.

The objective of the present work is to develop a mechanism and is mathematical description of heat transfer deterioration in film evaporators may occur without breaking the integrity of film is termed as boiling crises of the 2-type (dry out).

Materials and methods

The experimentation has been carried out on the specially designed unit, which allowed modeling of real downward co-current steam – highly concentrated sugar solution films. The installation consisted of a 9 m height vertical pipe of stainless steel A304, internal diameter of 30 mm, divided into 20 sections each 440 mm long.

The experimental pipe was encased into the outer pipe which served as a steam chamber for heating the inner experimental pipe. Maintaining constant steam temperature in the outer chamber provided a uniform along the pipe heating, and simultaneously modeled actual condition of heating in the industrial evaporators. The said sections were equipped with special pockets surrounding the lower part of each section with the drainage piping, allowing collecting condensate from the pipe sections and determining the distribution of heat flux along the pipe. The heating of the model tube was carried out with a dry saturated vapor. In the course of experiments, the temperature of the wall of the pipe was measured at 20 points, on each section by copper-constantan (type T) thermocouples.

Special probes positioned at each section allowed measurements of pressure head, concentration of solutions. In addition to the local data the following parameters were

measured: initial solution and steam inlet flow rates, temperatures, solution concentration, heating steam temperature. Such system of measurements provided a possibility to double check the accuracy of measurements.

The current film flow rate was determined based on the local measured values of concentration and compared with that determined by means of heat balance based on the amount of condensate collected on the previous sections, which was equivalent to the amount of evaporated solvent.

The independent inlet flow parameters allowed formation of flows with fully developed wavy structures thus modeling real flows in the industrial evaporators with taking into account a variety of factors influencing heat transfer and hydrodynamics of film flows.

Results and discussion

Concentration field modeling at constant film surface heat flux

For high viscosity liquid films, the predominant mode of their motion is laminar, so during the evaporation of water (solvent) within the boundary of the interphase surface a thin layer with a concentration greater than that in the bulk of the film is being formed. Since the concentration equalization mechanism is extremely slow due to molecular diffusion only, in the absence of mixing, the concentration gradient can be significant and the boiling temperature on the film surface should be higher than the boiling temperature calculated at the average concentration. In dense films, the value of physic- chemical temperature depression is commensurable with the total temperature head, so the latter factor becomes determinant in the decrease of the heat flux along the channel during the concentration of dense solutions.

To find out the influence of the uneven distribution of the concentration on the heat exchange, let us consider an element of the plane film, of saturated solution with the initial concentration C_o flowing along the vertical surface in the evaporation mode, Figure 1.

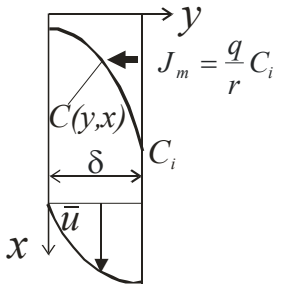

Figure 1. Schematics of the concentration distribution across the film at the evaporation from the interphase

In the process of concentration, the solvent evaporates, and the film thins at a rate $\frac{q}{r\rho}$. On the interfacial surface ($y=\delta$) the concentration increases forming a profile $C_i = C(\delta, x)$, therefore, as the solvent disappears, a normal mass flow of the dissolved component is being formed $J_m = \frac{q}{r} C_i$, which diffuses into the bulk of film due to molecular or turbulent diffusion. The equilibrium condition of the flows of the dissolved component on the interphase surface when taking account of the molecular diffusion only, will be expressed as:

$$-D_m \frac{\partial C(\delta, x)}{\partial y} = \frac{q}{r\rho} C(\delta, x) \ , \qquad (1)$$

where q – heat flux, r –specific heat of evaporation, ρ – liquid density, y,x – normal and longitudinal to the heat surface coordinate, δ – film thickness, D_m – molecular diffusion coefficient.

Equation (1) represents a boundary condition which holds on the interphase at $y=\delta$ and valid for the convection-diffusion equation

$$u\frac{\partial C(x,y)}{\partial x} = D_m \frac{\partial^2 C(x,y)}{\partial y^2}. \quad (2)$$

Since the transverse mass flux on the heated wall equals 0, then:

$$\frac{\partial C(0,x)}{\partial y} = 0.$$

Assuming an uniform velocity and concentration distribution on the inlet at $x = 0$

$$u(y,0) = \overline{u}\ ,\ C(y,0) = C_o. \quad (3)$$

If, further on, we assume that the effect of local velocity upon the left side of (2) may be accounted only by its mean value $\overline{u}(x)$, then the analytical solution of (1,2,3) will be [7]:

$$C(x,y) - C_o = 1 - \sum_{n=1}^{\infty} \frac{2\,\mathrm{Sin}\,\mu_n}{\mu_n + \mathrm{Sin}\,\mu_n\,\mathrm{Cos}\,\mu_n} \mathrm{Cos}\left(\mu_n \frac{y}{\delta}\right) \exp\left(-\mu_n^2 \frac{D_m x}{\overline{u}\,\delta^2}\right). \quad (4)$$

The respective characteristic equation for finding eigenvalues will be:

$$ctg\ \mu_n = \frac{\mu_n}{Pe_{mv}}, \quad (5)$$

where $-Pe_{mv} = \frac{q\,\delta}{r\,\rho\,D_m}$ – mass transfer Peclet number, expressed through the evaporation velocity $\frac{q}{r\,\rho}$.

The development of the concentration profiles along the evaporation wall is presented in Figure 2.

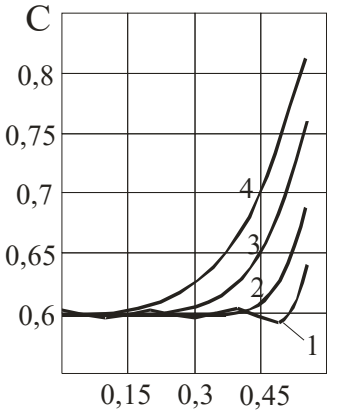

Figure 2. Concentration profiles in the downward film of concentrated sugar solution at a distance *x* from the evaporation channel
$1 - x = 0{,}1$ m; 2 – 0,8; 3 – 2,5; 4 – 5,
$Pe_{mv} = 1$; $CP_o = 60\%$; t = 80 °C;
$\Gamma_v = 0{,}15 \cdot 10^3 \frac{m^2}{s}$; $\nu = 3{,}92 \cdot 10^{-6} \frac{m^2}{s}$;
$\rho = 1260 \frac{kg}{m^3}$; $D = 1 \cdot 10^9 \frac{m^2}{s}$; $r = 2308 \frac{kJ}{kg}$;
$q = 5{,}14 \frac{kW}{m^2}$; $\mu_1 = 0{,}8603$; $\mu_2 = 3{,}4256$;
$\mu_3 = 6{,}4373$; $\mu_4 = 9{,}5293$; $\mu_5 = 12{,}6453$;
$\mu_6 = 15{,}7713$.

Interphase fluid concentration $C(x,\delta)$ may be found from (4) at $y = \delta$:

$$C(x,\delta) - C_o = 1 - \sum_{n=1}^{\infty} \frac{2 \operatorname{Sin} \mu_n \operatorname{Cos} \mu_n}{\mu_n + \operatorname{Sin} \mu_n \operatorname{Cos} \mu_n} \exp\left(-\mu_n^2 \frac{D_m x}{\overline{u}\, \delta^2}\right). \quad (6)$$

Modeling of concentration field at constant mass of dissolved component flux from film interface towards its bulk

The equations (4 and 6) are inconvenient in usage, since at every certain value of the heat flux and film thickness one should determine respective values of eigenvalues μ_n by (5) at the conditions of constant heat flux.

In real multi effect evaporators the heating surface is being heated by the steam, and therefore due to the increase of the film concentration, there is a respective growth in local physico-chemical temperature depression. This leads to the decrease in the positive temperature head, which eventually causes a gradual decrease, proportional to the positive temperature difference, of the local heat flux along the pipe. In the said conditions, it looks much more advisable to formulate the boundary conditions (1) in terms of qC_i constancy instead of constant *q*. This is equivalent to the constancy of the transversal mass flux of dissolve component $J_m = \frac{q}{r} C_i$, which holds true in a certain range of solution concentrations and temperature differences. Thus, (1) can be rearranged as follows:

$$-D_m \frac{\partial C(\delta,x)}{\partial y} = \frac{q}{r\rho} C(\delta,x) \approx \frac{J_m}{\rho} = const \ . \quad (7)$$

With the precise analytical solution of (2) with the boundary conditions (3,7) [7]:

$$C(\eta,\xi) = C_o + \frac{2J_m}{\rho D_m}\sqrt{\frac{D_m x}{\bar{u}}}\left\{\frac{1}{\sqrt{\pi}}\exp\left(-\frac{(\delta-y)^2\,\bar{u}}{4D_m x}\right) - \frac{(\delta-y)}{2\sqrt{D_m\frac{x}{\bar{u}}}}erfc\left(\frac{(\delta-y)}{2\sqrt{D_m\frac{x}{\bar{u}}}}\right)\right\} \quad (8)$$

]The results of calculations of (4) and (8) are given in Figure 3.

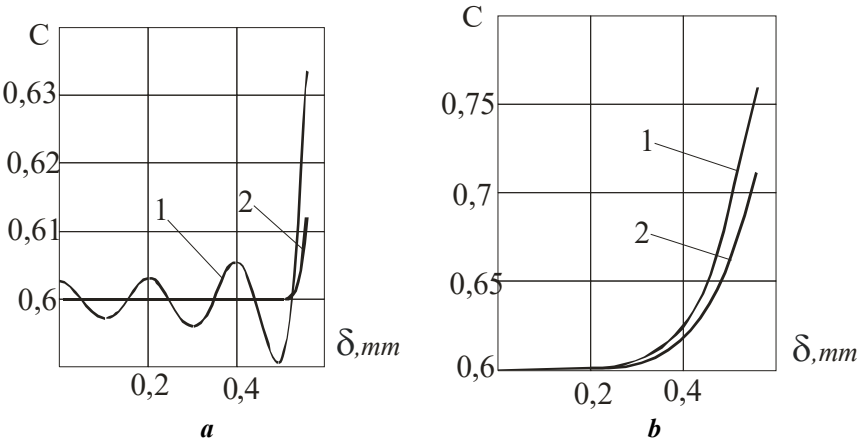

Figure 3. Calculated profiles of concentration across the film at the initial concentration of 60% DM:

$$\Gamma_v = 0{,}15\cdot10^{3}\,\frac{m^2}{s};\ \nu = 3{,}92\cdot10^{-6}\,\frac{m^2}{s};\ \rho = 1260\,\frac{kg}{m^3};\ D_m = 1\cdot10^{9}\,\frac{m^2}{s};$$

$$r = 2308\,\frac{\kappa J}{kg};\ q = 5{,}14\,\frac{kW}{m^2}.$$

a: x = 0,05 m; 1 – calculated by (4), 2 – by (8);
b: x = 2,5 m; 1 – calculated by (4), 2 – by (8).

In the dimensionless form (8) can be written as:

$$C(\eta,\xi) = C_o + \frac{2J_m\delta}{\rho D_m}\sqrt{\frac{4\xi}{Pe_m}}\left\{\frac{1}{\sqrt{\pi}}\exp\left(-\frac{(1-\eta)^2}{\frac{16\xi}{Pe_m}}\right) - \frac{(1-\eta)}{2\sqrt{\frac{4\xi}{Pe_m}}}erfc\left(\frac{(1-\eta)}{2\sqrt{\frac{4\xi}{Pe_m}}}\right)\right\}, \quad (9)$$

where $Pe_m = \frac{4\Gamma_v}{D_m}$ – diffusion Peclet number, Γ_v – volumetric liquid flux.

Fluid concentration on the interphace $C_i(\xi)$ can be found by (9) at $\eta = 1$.

$$C_i(\xi) = C_o + \frac{4J_m\delta}{\rho D_m\sqrt{\pi}}\sqrt{\frac{\xi}{Pe_m}}. \quad (10)$$

Modeling of critical heat transfer deterioration to films with developed wave structure at evaporation from film surface

The interphase surface of a dense viscous laminar film flowing down along a high vertical pipe is nearly smooth. Three-dimensional sickle-shaped swells periodically roll over the surface [8]. Under these conditions, the process of heat transfer is affected by the periodic perturbation of the film by wave-like rolls. These rolling swells mix the film and thus reduce the concentration on the interphase from its maximum value $C_i(\xi)$ to the mean in the bulk. Accordingly, the temperature distribution across the film also experiences periodic variations from the its initial profile, formed during the mixing process during the passage of the wave propagation, to the final, which is being formed at the moment of the next rolling swell approach. Given the fact that for low flow rates of the solution in the film and high viscosity of fluid, the film velocity profile after the perturbation initiated by the wave passage, transfers from the linear one to parabolic within a short section of a pipe. The heat transfer equation which determines the temperature field will be written:

$$\left[\left(\frac{\tau_i}{\nu\rho\delta}+\frac{g}{\nu}\right)\eta-\frac{g}{2\nu}\eta^2\right]\delta^3\frac{\partial\theta(\eta,\xi)}{\partial\xi}=a\frac{\partial^2\theta(\eta,\xi)}{\partial\eta^2}\ , \tag{11}$$

where $\eta=\frac{y}{\delta}$ – dimensionless transverse coordinates; $\xi=\frac{x}{\delta}$ – dimensionless longitudinal coordinates; τ_i – shear stress on the film surface; ν – cinematic viscosity coefficient, a – temperature conductivity, g –acceleration of gravity; $\theta(\eta,\xi)=\frac{t(\eta,\xi)-t_i(\xi)}{t_w-t_i(\xi)}$ – dimensionless temperature; t_w – wall temperature;

Approximate solution of (11) with the corresponding boundary conditions $\eta=0$, $\theta=1$; $\eta=1$, $\theta=0$, with the initial temperature distribution which is formed at the passage of a large wave at $\xi=\xi_m$ and is given as:

$$\theta(\eta,\xi_m)=\left(\frac{Pe}{4}\right)\frac{1}{D}\exp\left(-\frac{\xi_m}{D}\right)\left(\frac{\eta^2}{2}-\eta\right)+1\,, \tag{12}$$

is as follows [11]:

$$\theta(\eta,\xi)=\frac{Pe}{8}\left[\frac{R_1-1}{R}+\frac{Pe}{80DR}\frac{(16\rho g\delta+25\tau_i)}{(3\tau_i+2\rho g\delta)}\exp\left(-\frac{\xi_m}{D}\right)\right]\exp\left[\frac{\xi_m-\xi}{R}\right](\eta^2-\eta)-\eta+1, \tag{13}$$

where $D=\frac{Pe}{80}\frac{25\tau_i+16\rho g\delta}{3\tau_i+2\rho g\delta}$; $R=\frac{(7\rho g\delta+10\tau_i)}{(3\tau_i+2\rho g\delta)}\frac{Pe}{160}$; $R_o=\frac{4\tau_i+3\rho g\delta}{7\rho g\delta+10\tau_i}\frac{40}{Pe}$;

$R_1 = RR_o = \dfrac{\tau_i + \dfrac{3}{4}\rho g\delta}{3\tau_i + 2\rho g\delta}$; $Pe = \dfrac{4\Gamma_v}{a}$; $\xi_m = D\ln\left(\dfrac{Pe}{8D}\right)$ – distance at which $\theta(1,\xi_m) = 0$.

Under the conditions of tail film evaporators of the multi effect evaporation plants during the concentration of thick sugar syrups the characteristic values of positive temperature difference between the heating surface and film are being kept low. Therefore the heat flux and the co-current steam velocity are also low, even in case of long evaporative pipes. As a result, the shear stress on the interphase at the given conditions has little effect on the hydrodynamic parameters of the film. Under this condition, the movement of the film approximates the free downward flow on the vertical surface. In the case of free downward flow ($\tau_i = 0$), the above complexes D, R, R_o, R_1 can be written if the form:

$$D = \frac{Pe}{10},\quad R = \frac{7\,Pe}{320},\quad R_o = \frac{120}{7\,Pe},\quad R_1 = RR_o = \frac{3}{8}.$$

The temperature profile (13) transforms into :

$$\theta(\eta,\xi) = \left[\frac{40}{7}\exp\left(-\frac{10}{Pe}\xi_m\right) - \frac{25}{7}\right]\exp\left(\frac{320}{7Pe}(\xi_m - \xi)\right)\left(\eta^2 - \eta\right) - \eta + 1. \tag{14}$$

The dimensionless coordinate ξ_m at which $\theta(1,\xi_m) = 0$, can be found from the following:

$$\xi_m = 0,0223\,Pe. \tag{15}$$

During evaporation, the temperature on the film surface equals to that of the steam plus the value of physical-chemical depression, which is determined by the local dry matter concentration:

$$t_i(\xi) = t_{sat} + R_{dep}(\xi). \tag{16}$$

The relationship between the value of physical-chemical depression and local solution concentration $R_{dep}(\xi)$ may be expressed as a piecewise two-section approximation within the concentration intervals $0,37 < C < 0,75$ as:

$$R_{dep}(\xi) = 16,22\frac{T^2}{r}\left(\frac{C_i(\xi)}{a - bC_i(\xi)}\right). \tag{17}$$

And $0,75 < C < 0,9$ as:

$$R_{dep}(\xi) = \left(1156,9 - 6322C_i(\xi) + 1,3\cdot 10^4 C_i^2(\xi) - 11920C_i^3(\xi) + 4134C_i^4(\xi)\right)16,22\frac{T^2}{r}, \tag{18}$$

where $a = 0,62655$, $\sigma = 0,695$.

The temperature distribution within the film may be denoted as a function of the interphase temperature $t_i(\xi)$:

$$t(\eta,\xi) = t_i(\xi) + \left[t_w - t_i(\xi)\right]\theta(\eta,\xi), \tag{19}$$

or, making use of (16), it may be expressed through the saturated steam temperature t_{sat}:

$$t(\eta,\xi) = t_{sat} + (t_w - t_{sat})\theta(\eta,\xi) + R_{dep}(\xi)\left(1-\theta(\eta,\xi)\right) \quad . \tag{20}$$

The value of heat flux on the wall $q_w(\xi)$ can be found using (14, 20) keeping in mind that

$$q_w(\xi) = -\frac{\lambda}{\delta}\frac{dt(\eta,\xi)}{d\eta}\Big|_{\eta=0}$$

which leads to:

$$q_w(\xi) = \frac{\lambda}{\delta}\left\langle\left[\frac{40}{7}\exp\left(-\frac{10\xi_m}{Pe}\right) - \frac{25}{7}\right]\exp\left(\frac{320}{7Pe}(\xi_m - \xi)\right) + 1\right\rangle\left[t_w - t_{sat} - R_{dep}(\xi)\right], \tag{21}$$

where λ – liquid thermal conductivity.

Since ξ is measured from ξ_m, the expression for $R_{dep}(\xi)$ within the concentration range less than 75% ($C \le 0,75$) will acquire the form:

$$R_{dep}(\xi) = \frac{C_o + \dfrac{4J_m\delta}{\rho D\sqrt{\pi}}\sqrt{\dfrac{\xi-\xi_m}{Pe_m}}}{a - b\left(C_o + \dfrac{4J_m\delta}{\rho D\sqrt{\pi}}\sqrt{\dfrac{\xi-\xi_m}{Pe_m}}\right)}16,22\frac{T^2}{r}, \tag{22}$$

And within a range of $0,75 < C < 0,9$ –

$$R_{dep}(\xi) = \left(\begin{matrix}1156,9 - 6322C_i(\xi-\xi_m) + 1,3\cdot10^4 C_i^2(\xi-\xi_m) - 11920C_i^3(\xi-\xi_m) + \\ +4134C_i^4(\xi-\xi_m)\end{matrix}\right)16,22\frac{T^2}{r}$$

. (23)

As it follows from, in case of a significant shear stress on the interphse as a result of a stem velocity over the liquid film, the suppression of physical-chemical depression which is accounted for by the multiplier H_{dep} to the $R_{dep}(\xi)$ (22,23)

$$H_{dep} = \exp\left(-1,07\cdot10^{-2}\sqrt{We}\sqrt[3]{Pe}\right), \tag{24}$$

where $We = \dfrac{\rho_2 u^2 d}{\sigma}$ – the Weber number; u – steam velocity; σ – surface tension, ρ_2 – steam density; d – pipe diameter.

Having taken into account the effects of physical-chemical depression, its suppression by the co-current steam flow, expressed by (16, 22,23,24), the positive available temperature difference will determine the value of the local wall heat flux, which under above assumptions can be written as:

$$q_w(\xi)=\frac{\lambda}{\delta}\left\langle\left[\frac{40}{7}\exp\left(-\frac{10\xi_m}{Pe}\right)-\frac{25}{7}\right]\exp\left(\frac{320}{7Pe}(\xi_m-\xi)\right)+1\right\rangle\left[t_w-t_{sat}-R_{dep}(\xi)H_{dep}\right]. \tag{25}$$

Figure 4 depicts the calculated values of the cyclic, respective to the passages of successive large waves, changes of wall heat flux along a high vertical pipe (9 m long) on a section of 1 m long (between 4th and 5th m) to the highly concentrated sugar solution film at a regime of evaporation from free surface.

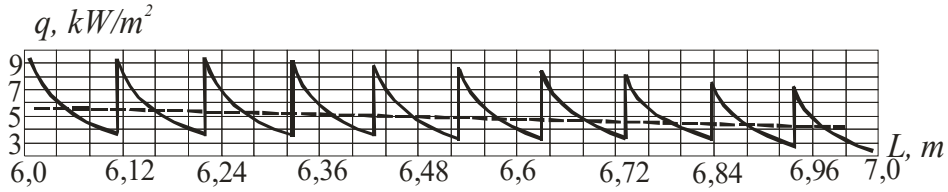

Figure 4. Profile of local values of wall heat flux along a high vertical pipe on the 1 m section (between the 4th and 5th m) to the highly concentrated sugar solufion flowing down in the regime of evaporation from the free surface.

Inlet fluid parameters: DM_n = 75,5 % ; Γ_v= 0,061 10^{-3} m^2/s;

u_2 – 3,8 m/s, t_w = 115 °C, t_{sat} = 100 °C. $\lambda_{bw}=0,12m$

The averaging of the heat flux values within the successive large waves has been carried out within the interval $\xi_v-\xi_m$ for each wave cycle :

$$\overline{q}_w=\frac{1}{\xi_v-\xi_m}\int_{\xi_m}^{\xi_v}q_w(\xi)d\xi\,. \tag{26}$$

In (26) the parameter ξ_m has been calculated as per (15), whereas – $\xi_v=\xi_m+\frac{\lambda_{bw}}{\delta}$, where λ_{bw} – the length of big waves and $\delta=\sqrt[3]{\frac{3\Gamma_v\nu}{g}}$ – represents the calculated film thickness. The length of large waves for the free down flow of cold water films in 25–32 mm diameter pipes ranged from 0.1 to 0,14 m. A similar result has been found at free film flow of concentrated apple syrup on a vertical flat surface.Making use of the above, when calculating the heat flux distribution along the pipe, the interval $\xi_v-\xi_m$ is calculated based upon the condition of the large waves length $\lambda_{bw}=0,12m$. The character of the heat flux distribution is practically solely determined by the distribution of the useful temperature head as a function of the physical - chemical temperature depression value, which, in turn, is a function of concentration of the solution on the interphase boundary, Figure 5.

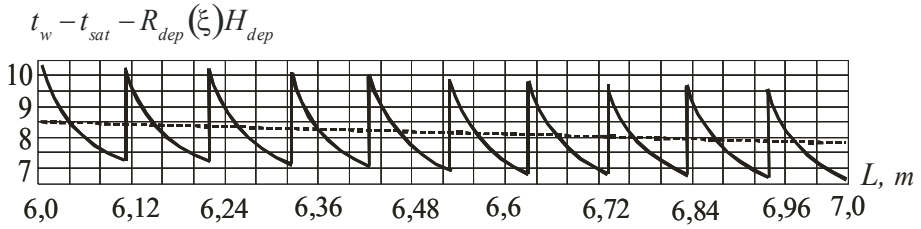

Figure 5 . Temperature head distribution along the 9 m long pipe on the section of 1 m long (between 4th and 5th m) at the regime of evaporation from the interphase surface.
Inlet parameters – are the same as in Figure 4.

It is quite clear that due to the evaporation, there will be a certain film concentration growth along the flow as well as across the film. Moreover, there will be a noticeable concentration growth within a length of a single inter wave cycle, which is shown in Figure 6.

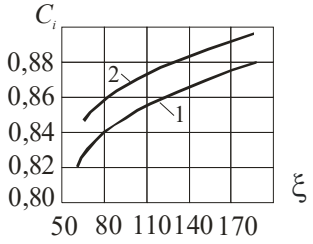

Figure 6. Film free surface concentration distribution C_i within a single wave cycle.
Data presented in Figure 6, are obtained for the flow in 9 m high pipe , curve 1– at a 4 m distance from the pipe inlet, relates to the 1st cycle as per data in Figure 4,5. Curve 2– 5 m distance, relates the 10th cycle.

The calculation results of the film mean thickness, liquid viscosity and mean solution concentration within the pipe section from 4m to 9m are presented in Figure 7, a, b, c.

The comparison of the experimental and calculation data related to the concentration of sugar solutions in the vertical pipes within the section between 4m to 9 m is presented in Figure 8.

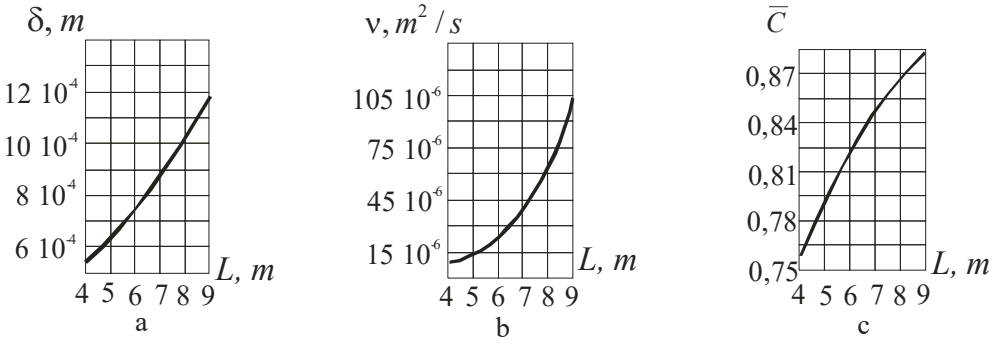

Figure 7. Mean values of the film thickness (a), viscosity (b) and solution concentration (c) within the pipe section from 4m to 9m.
Inlet parameters – are the same as in Figure 4,5.

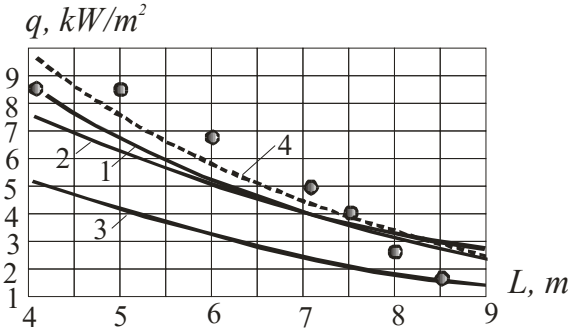

Figure 8. Comparison of the calculated and experimental data.
Initial parameters of the solution are:
Sugar solution concentration 75,5 % DM,
$\Gamma_v = 0{,}061\ 10^{-3}$ m²/s, u = 3,8 m/s, t_w = 115 °C, t_{sat} = 100 °C, $\lambda_{bw} = 0{,}12\,m$.

As it may be seen from Figure 8, the line 1 calculated as per (23-26) shows the same trend as the experimental data do, but deviates significantly form the experimental data, especially on the initial sections of the pipe where the error reaches 25 % (within 4th –5th m).

Line 2 – is calculated based upon taking into account the mean over the section concentration $\overline{C}$ with the further calculation of physical-chemical depression and its reduction effect upon the heat transfer:

$$q = \frac{\lambda}{\delta}\left(t_w - t_{sat} - R_{dep}\left(\overline{C}_{ni}\right)\right),$$

where $R_{dep}\left(\overline{C}_{ni}\right) = \left(1156{,}9 - 6322\overline{C}_{ni} + 1{,}3\cdot 10^4\,\overline{C}_{ni}^{\,2} - 11920\overline{C}_{ni}^{\,3} + 4134\overline{C}_{ni}^{\,4}\right) 16{,}22\dfrac{T^2}{r}$, $\overline{C}_n$ – mean at every section fluid concentration,

$$\overline{C}_n = \frac{\overline{C}_{n-1}\Gamma_v^{n-1}}{\Gamma_v^{n-1} - \dfrac{\overline{q}_n\delta_n\left(\xi_v - \xi_m\right)}{\rho\, r}}, \qquad (27)$$

$\overline{C}_{n-1}$ – mean fluid concentration at the section inlet, Γ_v^{n-1} – mass flow wetted perimeter, $\overline{q}_n$ – mean heat flux on a section (26). As it follows from Figure 8 , this methodology does not lead to more close correlation of the data. The deviation on the initial pipe sections grows even bigger as compared to the line 1.

Line (3) – is calculated based on the mean interphase fluid concentration $\overline{C}_{ni}$.

$$q = \frac{\lambda}{\delta}\left(t_w - t_{sat} - R_{dep}\left(\overline{C}_{ni}\right)\right),$$

where $R_{dep}\left(\overline{C}_{ni}\right) = \left(1156{,}9 - 6322\overline{C}_{ni} + 1{,}3\cdot 10^4\,\overline{C}_{ni}^{\,2} - 11920\overline{C}_{ni}^{\,3} + 4134\overline{C}_{ni}^{\,4}\right) 16{,}22\dfrac{T^2}{r}$,

$$\overline{C}_{ni} = \frac{1}{\xi_v - \xi_m}\int_{\xi_m}^{\xi_v} C_i\left(\xi\right)d\xi = \overline{C}_{n-1} + \frac{8Pe_m J_m \delta}{3\sqrt{\pi}\ \rho D_m\left(\xi_v - \xi_m\right)}\left(\sqrt{\left(\frac{\xi_v}{Pe_m}\right)^3} - \sqrt{\left(\frac{\xi_m}{Pe_m}\right)^3}\right).$$

Despite of its greatest complexity, this calculation method gives the worst congruency with the experimental data. This may be explained by not taking into consideration the effect of physical-chemical depression reduction can be calculated by (24).

Line (4) – is calculated by the interval approximation method with further taking in account the reduction effect of co-current steam flow by the equations (28) taken as per mean fluid concentrations at sections $\overline{C}_n$ (27)

$$q = \alpha\left(t_w - t_{sat} - H_{dep}R_{dep}\left(\overline{C}_n\right)\right)$$

$$\frac{\alpha}{\lambda}\left(\frac{\nu^2}{g}\right)^{1/3} = 1{,}12\,\mathrm{Re}^{-1/3}\left(0{,}85 + 0{,}01\,Pe^{0{,}2} + 4{,}5\cdot10^{-4}\,Pe^{0{,}86}\,\mathrm{Pr}^{-0{,}2}\right)K_w K_{boil} K_{Ld}, \qquad (28)$$

where $K_{Ld} = \left\{1 + 0{,}06\left(\frac{\nu}{\nu_o + \nu}\right)\left[1 - \exp\left(-0{,}05\,L^3\right)\right]\right\}\left(\frac{d}{d_o}\right)^{0{,}35 - 0{,}06\left(\frac{d}{d_o}\right)}$;

$K_w = \sqrt{1 + \left[7{,}5\cdot10^{-6}\,\mathrm{Re}_2\left(\rho/\rho_2\right)^{0{,}2}\right]^2}$, $K_{boil} = 1$; $\mathrm{Re} = \frac{4\Gamma_v}{\nu}$; $\mathrm{Re}_2 = \frac{u\,d\,\rho_2}{\mu_2}$;

μ_2 – steam viscosity dynamic coefficient, $Pa\cdot s$;

ν_o – water viscosity kinematic coefficient 100 °C; L – pipe length, m;

α – the heat transfer coefficient (HTC), $\frac{W}{m^2 s}$; d_o – 0,02 m.

As one may see, the proposed method renders the best congruity of the calculated and experimental data.

Conclusions

1. The proposed model of heat transfer in the liquid films as a process of periodic destruction of the surface layer of the super-high concentration solutions by large waves, which at high viscosity have the form of inflows, adequately reflects the processes of heat transfer deterioration to dense films in long channels in the mode of evaporation from the interphase surface.
2. The recommended calculation correlations and methodology allow obtaining data closely conforming to those found experimentally and thus may be recommended to be used in the engineering calculations of the industrial film evaporators.
3. The main reason for the deterioration of heat transfer to dense films in the process of concentration is the excess of the value of physical-chemical temperature depression on the interphase boundary over the mean temperature head value due to the uneven distribution of concentration. In a lesser degree, the intensity of the heat transfer is influenced by the growth of the film thickness and the drop in the dense solution thermal conductivity as the fluid concentration increases.
4. Recirculation of a dense solution in film evaporators on the one hand leads to a deterioration of heat transfer due to the growth of the average length of the concentration pipe, and on the other – it promotes the activation of the wave process and disruption of a highly concentrated layer on the interphase surface, which causes the intensification of heat transfer.

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Modelling of the hydrodynamic conditions throughout liquid system treatment by alternating impulses of pressure

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Abstract

Introduction. The purpose of this scientific work is to research the influence of the application of alternating impulses of pressure throughout treatment of liquid solutions by the numerical modelling.

Materials and methods. The volume parametric imitation and visualization, modelling methods, math modelling methods were used for the description of the conditions at the working parts of the rotary pulsed apparatus during the liquid treatment. Experimental investigations of liquid samples were carried out with using potentiometry laboratory measurement procedure.

Results and discussion. In this paper, it is established that the local values of pressure in the sector of input of water and water systems and the output of the water systems from the gaps vary: at the external surface of the internal rotor from -50 to +300 kPa; at the external stator surface from -150 to 100 kPa; at the inner stator surface from +40 to -120 kPa; at the inner surface of the external rotor from +100 to -100 kPa. During the last values cavitation and adiabatic boiling can be present.

Throughout the water and water solutions treatment and during the processes of mixing liquid associated components in the conditions of hydrodynamic fluctuation as alternating impulses of pressure characterized the changing of pressure: ΔP = 350 kPa near an outside surface of an interior spinning rotor; ΔP = 250 kPa near an outside stator surface; ΔP = 160 kPa near an interior stator surface; ΔP = 200 kPa near an interior surface of an outside spinning rotor.

By the consequences of the computation was established that the principal values of speeds of shift of a stream emerge in RPA with coaxial clearances between first rotors, stator and second rotor 100 mkm.

Conclusions. Throughout the calculations was found the values of pressure changing in working chamber of rotary-pulsating apparatus between coaxial cylinders «rotor-stator-rotor» system. These give us the possibility to receive the liquids with necessary and required physical and chemical properties and parameters by the no reagent influence and to control this processes.

Introduction

At the present time a great variety of technological processes of foodstuff manufacture have to reduce energy consumption and to intensify industrial modes.

One of the way to solve this problem is to employ innovative nonstandard energy and resource saving and inexpensive equipment and new optimized modes of treatment.

There are many methods and processes of water treatment to obtain water and water solutions with necessary physical and chemical parameters and properties which require for the manufacturing.

They are including: acoustic treatment, the electromagnetic pulse effect of the low-frequency field, cavitations processing, emitting treatment (ultraviolet, ionizing, infrared), hydrodynamic effects [1–3].

The method of discrete-pulsed input of energy can power structural transformations in difficult liquid systems on micro- and nanolevel and gives possibility to initiate physical and chemical transformations in these complex systems.

The main effects of the discrete-pulsed input of energy are effects which connected with increase of velocity of association of a continuous phase, power of pressure of shift, cavitations, the effect of explosive boiling, collective effects in assembly of vials, crossness of an interphase surface in gas-liquid bubbly medium, action of hydrodynamic oscillations, alternating impulses of pressure.

A great number of mass engineering processes such as: mixing, homogenization, crushing, dispersion, activating, emulsification, etc are exhausted in rotary pulsed apparatus of different type.

The main effects of the discrete-pulsed input of energy are realising in these types of apparatus.

To intensify mixing of associated mediums it is necessary to use rotary pulsed apparatus. In such equipment the treatment of liquid mediums occurs with the passage throughout thin annular clearance [4].

This clearance is formed by the surfaces of coaxial cylinders which turn around common axis (rotors) and inexperienced cylinder (stator).

There are many slits on the rotors and stator. During the treatment slits can coincide on the rotors and stators. Significant pressures of the shift and microcirculation streams emerge as a result of the treatment of liquid heterogeneous solutions in working chamber and parts of the apparatus.

Self-oscillation mode can occur throughout the treatment of liquid mediums at rotary pulsed apparatus. The oscillations of velocities and pressures in mediums which processed are characterizing self-oscillation mode [PI UA № 117998, A method for preparation of disinfectant].

High energy transitional hydro-mechanical influence on liquid mediums and solutions in rotary pulsed apparatus conducts to transformation of structural formation and in the same time there is no intensive destruction of macromolecules and associates.

To optimize the process of hydrodynamic treatment it is necessary to define the level of power influence on the liquid mediums and solutions for indispensable transformations which can provide predictable physical and chemical parameters.

The main factors and driving forces that cause them are the stresses of the pressures of shift of a stream, the speeds of shift of a stream, alternating impulses of pressure.

The main features of the technological mediums processing are:

– the mechanical influence on the particles of a heterogeneous mediums consisting of shock and abrasive loads during contact with the working parts of the rotary pulsed apparatus;

- the hydrodynamic effect, which manifests itself in significant tangential stresses in the fluid, developed turbulence, pressure pulsations and fluid flow speeds;
- the hydroacoustic influence on the liquid system is carried out by the microscale pressure pulsations, intense cavitation, shock waves and nonlinear acoustic effects [5, 6].

For a complete description of the mixing process and the treatment modes, the first necessary condition is the establishment of qualitative and quantitative coherency between the properties and the physical and chemical parameters of the initial components.

It is significant to establish the coherency between technological modes of carrying out the mixing process and the treatment modes, the design and constructor features of the working apparatus and the properties and physical and chemical parameters of the resulting mixtures.

It is important to use the parameters that should directly reflect the nature of the energy effect on the liquid medium. It is also necessary to use parameters reflecting the nature of the energy action on the particles of substances.

Accordingly, the essential conditions are:

- the establishing of connection between the constructional parameters of the rotary pulsed apparatus with the energy effect, which is achieved at the same time;
- the determination of the dependence of the main technological parameters of the treatment process on the intensity of the energy impact and influence.

On the basis of the numerical experiment and analytical calculation, the main constructional parameters of the apparatus were found which influence the intensification of the processes of mixing liquid components and treatment of the liquid technological mediums.

The purpose of this scientific work is to research the influence of the application of alternating impulses of pressure throughout treatment of liquid solutions by the numerical modelling.

Materials and methods

Materials

Liquid solutions and systems: water, alcohol, water-alcoholic solutions and mixtures in a wide range of concentration (percentage of alcohol in mixtures was varied from 5 to 90%), distilled aqua, hydroponic [7], hydroponic with fertilizers [8] were used for experiments.

Experimental installation

The object of this scientific research work was rotary pulsed apparatus in which liquid solutions treat by alternating impulses of pressure, the speeds of shift of a stream, pressures of shift of a stream. Rotary pulsed apparatus was the cylindrical type with the working parts «rotor-stator-rotor» [9].

Methods

General scientific methods and special methods, such as potentiometry were used for the analyzing of the results of research work [10].

The volume parametric imitation and visualization, modelling methods, math modelling methods were used for the description of the conditions at the working parts of the rotary pulsed apparatus during the liquid treatment.

Experimental investigations of liquid samples were carried out with using potentiometry laboratory measurement procedure [11].

For the description of physical and chemical parameters of liquid samples of water and solutions which obtained throughout the experimental investigations, chemical methods described in singular literature are used [12].

For the reception related data, liquid samples of water and solutions were analyzed not less than three times with the following statistical processing [13].

Results and discussion

Numerical simulation model

The numerical simulation and visualization was employed for hydrodynamic computation of the treatment and mixing processes in working volume (chamber) of the rotary pulsed apparatus (RPA).

For the choice of numerical model of fluid flow in the «rotor-stator-rotor» system of the RPA, it was suggested that the current in the prevailing case is two-dimensional.

The heterogeneous stream was considered to be a homogeneous medium with the effective thermophysical properties.

To consider the dynamics difficulty, the horizontal section of the working parts of the RPA, perpendicular to the axis of the «rotor-stator-rotor» system, was selected. This section has slits on the surfaces of the first rotor, stator and second rotor. Also this section consists of the left and right parts of the rotors.

In addition that takes place geometrical and physical periodicity of the processes in the geometrical similar sections. That's why border conditions at left and right sides of the section are considered as a periodic.

In accordance with [14], the dimensionless system of fluid dynamics equations was chosen. For calculations, the dimensionless system of fluid dynamics was recorded in polar coordinates [15].

The midpoint of this section locates on the axis of the frame «rotor-stator-rotor» system.

Dimensionless equation system (1)–(5):

$$\frac{1}{R}\frac{\partial(RV)}{\partial R}+\frac{\partial\Omega}{\partial\theta}=0 \tag{1}$$

$$\frac{\partial V}{\partial H}+\frac{1}{R}\frac{\partial(RV^2)}{\partial R}+\frac{\partial(V\Omega)}{\partial\theta}-\Omega^2R=-\frac{\partial P}{\partial R}+\frac{2}{\mathrm{Re}R}\frac{\partial}{\partial R}\left(R\beta\frac{\partial V}{\partial R}\right)-$$
$$-\frac{2}{\mathrm{Re}R}\beta\left(\frac{\partial\Omega}{\partial\theta}+\frac{V}{R}\right)+\frac{1}{\mathrm{Re}R^2}\frac{\partial}{\partial\theta}\left(\beta\frac{\partial V}{\partial\theta}\right)+\frac{1}{\mathrm{Re}}\frac{\partial}{\partial\theta}\left(\beta\frac{\partial\Omega}{\partial R}\right); \tag{2}$$

$$\frac{\partial\Omega}{\partial H}+\frac{1}{R^2}\frac{\partial(R^2\Omega V)}{\partial R}+\frac{\partial\Omega^2}{\partial\theta}+\frac{\Omega V}{R}=\frac{1}{R^2}\frac{\partial}{\partial\theta}\left[-P+\frac{2}{\mathrm{Re}}\beta\left(\frac{\partial\Omega}{\partial\theta}+\frac{V}{R}\right)\right]+$$
$$+\frac{1}{\mathrm{Re}R^3}\frac{\partial}{\partial R}\left[R\beta\left(R^2\frac{\partial\Omega}{\partial R}+\frac{\partial V}{\partial\theta}\right)\right]; \tag{3}$$

$$\frac{\partial \vartheta}{\partial H}+\frac{1}{R}\frac{\partial (R\vartheta V)}{\partial R}+\frac{\partial \vartheta \Omega}{\partial \theta}=\frac{1}{\mathrm{RePr}}\left[\frac{1}{R}\frac{\partial}{\partial R}\left(\Lambda R\frac{\partial \vartheta}{\partial R}\right)+\frac{1}{R^2}\frac{\partial}{\partial \theta}\left(\Lambda\frac{\partial \vartheta}{\partial \theta}\right)\right]+\beta S^2 \qquad (4)$$

$$S=\left[2\left(\frac{\partial V}{\partial R}\right)^2+2\left(\frac{\partial \Omega}{\partial \theta}+\frac{V}{R}\right)^2+\left(\frac{1}{R}\frac{\partial V}{\partial \theta}+R\frac{\partial \Omega}{\partial R}\right)^2\right]^{0,5} \qquad (5)$$

The adduction to the dimensionless form of the equation system made by the changing:

$$V=\frac{v_r}{\omega_0 r_0};\ \Omega=\frac{\omega}{\omega_0}\ ;\ R=\frac{r}{r_0}\ ;\ H=\tau\omega_0;$$

$$P=\frac{(p-p_0)}{(\rho\omega_0 2r_0^2)};\quad \vartheta=\frac{(T-T_0)\rho Cp}{(\omega_0\mu_0)}$$

$$\mathrm{Re}=\frac{\rho\omega_0\times r_0^2}{\mu_0};\qquad \mathrm{Pr}=\frac{c_p\mu_0}{\lambda_0}\ ;$$

p_o – the pressure of the medium behind the working chamber of the rotary pulsed apparatus;

T_o – the temperature of the medium behind the working chamber of the rotary pulsed apparatus;

$\omega=\frac{\vartheta}{r}$ - angular velocity;

ω_0 – angular velocity of the rotor spinning;

r_0 – radius of the internal surface of the internal stator;

$\beta=\frac{\mu_{ef}}{\mu_0}$; $\Lambda=\frac{\lambda_{ef}}{\lambda_0}$;

μ_{ef} – effective values of the viscosity coefficient;

λ_{ef} – effective values of the coefficient of thermal conductivity;

μ_0, – conditional scale of the viscosity coefficient

λ_0 – conditional scale of the coefficient of thermal conductivity.

Since rotary-pulsating apparatuses belong to periodic devices, it is necessary to pay attention to the fact that there is a geometrical periodicity of the design of the «rotor-stator-rotor» system of working chamber.

In this connection, the frequency of changes in the dynamic characteristics of the fluid flow through the working area of the RPA is observed. When the RPA mode is set, the movement of the fluid is repeated after rotating the rotors at a periodic angle $\Delta\theta$.

To solve this assigned problem, a certain segment was selected that periodically repeats the angle $\Delta\theta$.

The segment contained a fragment of the «rotor-stator-rotor» system with a slits on the surfaces of the rotors and stator also clearance between these working elements of the system.

The pressure difference between the input and the output liquid solutions at the working volume (chamber) before and after treatment is $\Delta P = 50$ kPa.

Geometric sizes of working elements were set according to constructional and design dimensions of RPA.

The speed of rotation of the rotor was given $n = 48$ sec^{-1}. In the calculation it was considered that the flow regime of the liquid in the RPA is turbulent, so for this case RNG k-ε model of turbulence was chosen [16].

The system of equations was reduced to dimensionless form.

By the volume three-dimensional parametric imitation visualization modelling processes, mathematical and numerical modelling was found that the value of the linear speeds of a stream should be within 20 m/s for the first rotor and 25 m/s, for the second rotor.

The investigation of the structure of the stream, and the vortical nature of the fluid movement, was performed by numerical simulation of the flow dynamics based on the Navier-Stokes equations.

The main factors of the flow structure is determined by the fields of pressures, speeds, accelerations [17].

The changes of the pressure in different points of the working volume (chamber) have complicated pulsating character.

For the numerical simulation were selected different positions of the «rotor-stator-rotor» system of working chamber.

It was selected for calculations the next points:

- on the external surface of the internal rotor,
- on the external stator surface,
- on the inner stator surface,
- on the inner surface of the external rotor.

The subsequently positions in working volume (chamber) between coaxial cylinders of the «rotor-stator-rotor» system were selected:

- open slit;
- half closed slit;
- half open slit;
- closed slit.

Investigation of alternating impulses of pressure

The profile of pressure fields in working volume between coaxial cylinders of the «rotor-stator-rotor» system during the ope *9* n slit are shown at the Figure 1.

It was established that speeds of shift of a stream should be equal to $2{,}0 \cdot 10^5 s^{-1}$ for the first rotor and $2{,}5 \cdot 10^5 s^{-1}$ for the second rotor.

Such values of the speeds of shift of a stream make available to intensive mixing and particle movement in continuous phase – water.

The value of pressure of shift of a stream must be 220 Pa for the first rotor and 230Pa, for the second rotor.

The visualization are showed the pressure fields in the first moment of time during the input of liquid components or solutions into a working chamber through the slits on the first rotor surface, stator surface and second rotor surface and among clearances between first rotor, than stator and second rotor at the certain segment.

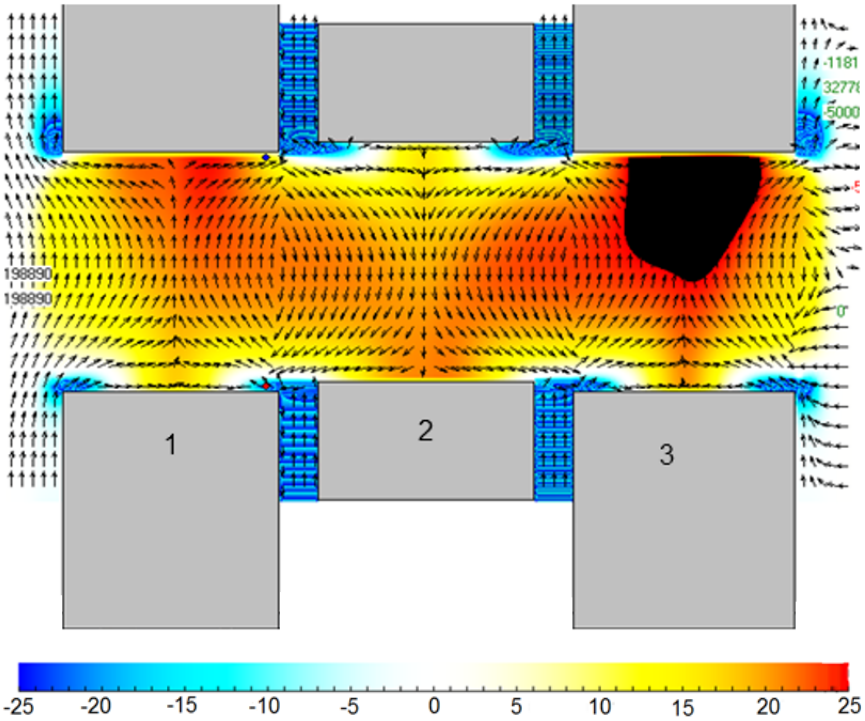

Figure 1. The profile of pressure fields in working volume (chamber) between coaxial cylinders (open slit): 1 – first rotor; 2 – stator; 3 – second rotor

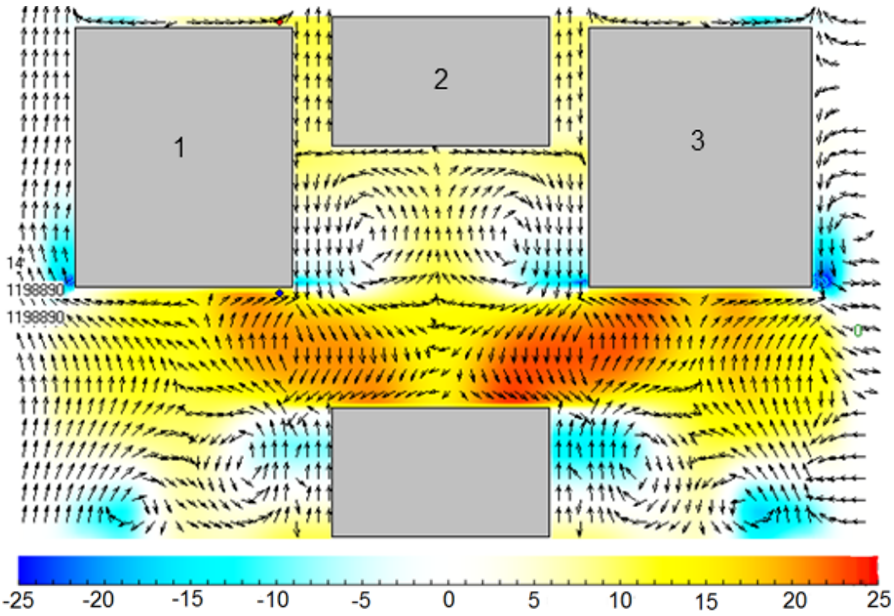

Figure 2. The profile of pressure fields in working chamber between coaxial cylinders (half open slit): 1 – first rotor; 2 – stator; 3 – second rotor

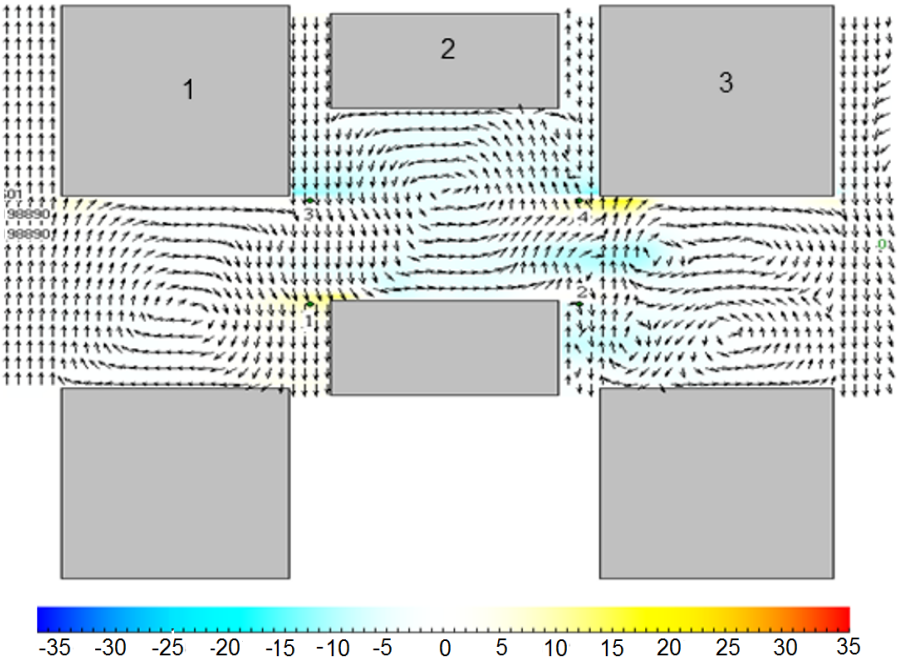

Figure 3. The profile of pressure fields in working chamber between coaxial cylinders (half closed slit): 1 – first rotor; 2 – stator; 3 – second rotor

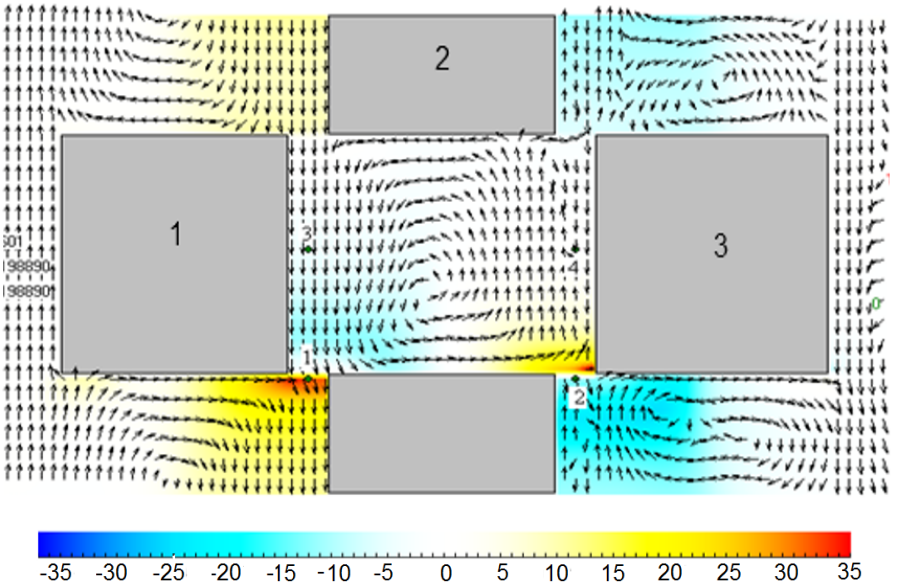

Figure 4. The profile of pressure fields in working chamber between coaxial cylinders (closed slit): 1 – first rotor; 2 – stator; 3 – second rotor

Based on the results of the analysis of the calculations obtained, it was found that the reducing of the clearance between the external and internal rotors and the stator leads to an increase in the depth of the negative impulse of pressure.

Such impulses of pressure contribute to the intensification of the instantaneous mixing process, with the exception of the contact of the components before entering directly into the working area of the RPA. It is important factor for mixing of the specific chemical substances which react instantly.

The mass transfer intensification, in turn, affects the speed of the process of hydration, structuring and association of the polar liquids as alcohols and water.

The local values of pressure in the sector of input of water and water systems and the output of the water systems from the gaps vary:

- at the external surface of the internal rotor from -50 to +300 kPa;
- at the external stator surface from -150 to 100 kPa;
- at the inner stator surface from +40 to -120 kPa;
- at the inner surface of the external rotor from +100 to -100 kPa.

During the last values cavitation and adiabatic boiling can be present [18].

Throughout the water and water solutions treatment and during the processes of mixing liquid associated components in the conditions of hydrodynamic fluctuation as alternating impulses of pressure characterized the changing of pressure:

- $\Delta P = 350$ kPa near an outside surface of an interior spinning rotor;
- $\Delta P = 250$ kPa near an outside stator surface;
- $\Delta P = 160$ kPa near an interior stator surface;
- $\Delta P = 200$ kPa near an interior surface of an outside spinning rotor.

Investigation of Speed of shift of a stream and pressure of shift of a stream

Important technical parameter such as speed of shift of a stream (Figure 5) was recognized for treatment of liquid solutions with the appliance of the alternating impulses of pressure.

By the consequences of the computation was established that the principal values of speeds of shift of a stream emerge in RPA with coaxial clearances between first rotors, stator and second rotor 100 mkm.

These demanding hydrodynamic conditions give the possibility to treat water system and water solutions [19] with the initialization of the formation of structure and intermolecular interacting such as forming three-dimensional framework from the hydrogen bonds. At a molecular scale, molecular dynamic simulation is an appropriate tool for analyzing these static and dynamic properties; as it provides a direct path from microscopic to macroscopic properties [20].

The nature and velocity of many physical and chemical processes which take place in such associated systems transforms.

Besides, the activity of the water depends from the transformations and hydrogen bonds which can form between molecules.

The changing of physical and chemical properties and parameters of pure water and water solutions has been established during the treatment with appliance of hydrodynamic fluctuation [21].

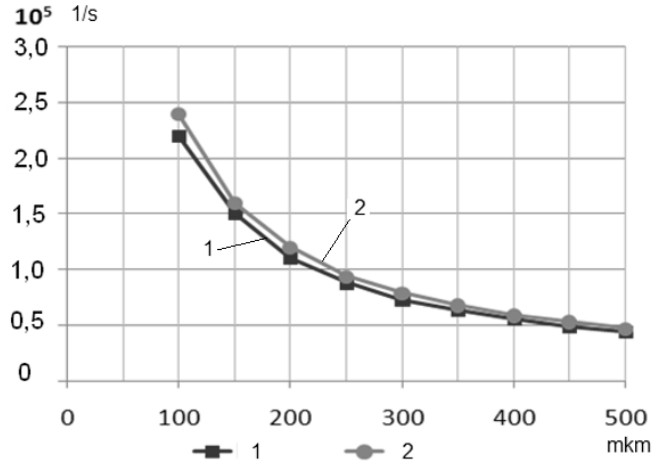

Figure 5. Profile of changes speeds of shift of a stream from the clearances between coaxial cylinders: 1 – first rotor; 2 – second rotor

By the results of the calculation was established that the largest values of pressure of shift of a stream emerge in RPA with coaxial clearances between rotors and stator 100 mkm Figure 6.

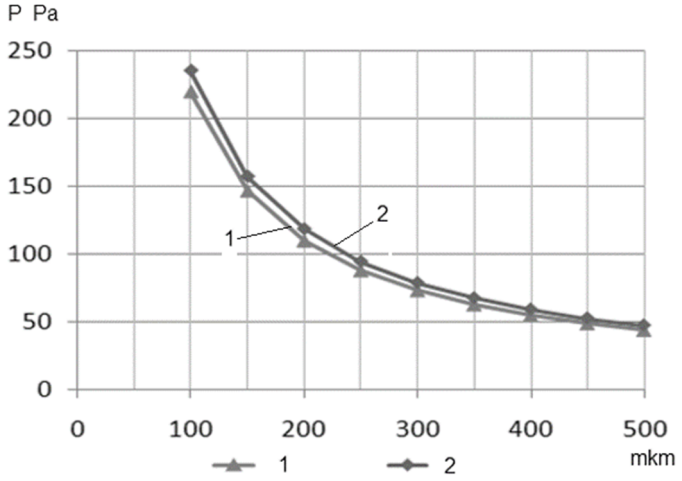

Figure 6. Profile of changes of pressure of shift of a stream from the clearances between coaxial cylinders: 1 – first rotor; 2 –second rotor

It was established that appliance of the alternating impulses of pressure for water solutions treatment give possibility to decrease redox potential on 20–70%, to increase the potential of hydrogen on 13–17%, to decrease mass of the dissolved oxygen on 50–55%. [22]

Conclusions

The application of alternating impulses of pressure throughout treatment of liquid solutions can influence on the physical and chemical parameters of the liquid systems by the hydrodynamic power.

Throughout the calculations was found the values of pressure changing in working chamber of rotary-pulsating apparatus between coaxial cylinders «rotor-stator-rotor» system. These give us the possibility to receive the liquids with necessary and required physical and chemical properties and parameters by the no reagent influence and to control this processes.

A detailed analysis of experimental data showed that the use of alternating impulses of pressure for treatment liquid solutions can be appropriate for processing in food engineering.

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Modeling of the process of kneading the yeast dough by cam operating elements

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Abstract

Introduction. A mathematical model was developed and simulation modeling of the process of kneading the yeast dough by cam operating elements was carried out.

Materials and methods. The conditions of the contact interaction of the material with the working elements and the chamber of kneading, as well as the value of the dough structural-mechanical characteristics were specified. During the simulation of the kneading process, the angular position of the cam element was changed from 90° to 585°.

Results and discussion. The scheme of the mathematical modeling of the process of mixing of the yeast dough in a dough machine of continuous action is developed. Based on the results of simulation of the mixing process, cam operating elements, the distribution of strain of displacement and dissipation of yeast dough in the working chamber were obtained. As the angle of the position (90° to 360°) of the cam element increases on the shaft, there is an increase in the shear stress. The greatest indices of shear stress occur in the area of cam clamping elements and in the contact area of the cam with the walls of the case, numerical values reach within 7000–8000 Pa. For the rest of the camera, the displacement stress reaches 1000–3000 Pa. Distribution of dissipation shows that in parts of the working chamber there is the formation of heat in the area of flow. With the increase of the angle of the cam (from 180° to 585°) of the cam element, there is a gradual increase in temperature. At the site of mixing 12 pairs of cams, the temperature of the yeast dough increases by almost 5 °C. Taking into account that before the simulation, the initial temperature reached t=30 °C, and upon completion of the mixing process did not exceed 35 °C, the pastry preparation parameters were observed. The greatest heat release occurs in the area of the cam clamping elements.

The results of mathematical modeling are confirmed by physical experiments on a test dough mixing machine of continuous action, an error within 5%.

Conclusions. The proposed simulation scheme allows us to investigate the process of mixing the yeast dough according to various technological parameters. The obtained results give the initial data for the choice of rational parameters of the process of mixing the yeast dough by the cam working elements.

Introduction

Mathematical modeling is an important tool in scientific research, but previously it was not used during the study of the process of mixing the yeast dough [18] by cam operating elements. The cam elements are gaining widespread acceptance, we have carried out a series of experimental studies that prove their effectiveness during the kneading process. During the viscous flow, the deformation is proportional to the stress imposed by Newton's law, and after the removal of the load is not restored [1–2]. Plastic deformation is created under stress that exceeds a certain limit value (the boundary of flowability), to which the material behaves as visco-elastic [4].

During mixing flour with water, the components of the flour form a hydrated bonded mass - a dough. Hydrated medium, which is a dough, the presence in this mass of introduced fermentable microflora is triggered by a system of complex biochemical, microbiological, colloidal and other processes [5–6].

Physical-mechanical processes take place at the dip under the influence of the master body, which mixes particles of flour, water, yeast suspension and solutions of raw materials, providing the interaction of all the constituents of the components of the formulation. By numerical studies it was found that an increase of the mechanical effect on the dough during the dipping affects its rheological properties [7–8].

The cam working elements are becoming more widely used, but almost non-exploratory, requiring in-depth study and detailed analysis. By way of a critical analysis of literary sources on the subject of the process of mixing, the directions of development and improvement of this issue were identified, thus a deep and systematic study requires the problem of qualitative and intensive mixing of yeast dough in continuous-dough machines of continuous action [9].

A scientific review of constructions of dough machines and their components, has revealed the main advantages and disadvantages of design solutions in the design and operation of continuous machines of continuous action [12]. The main disadvantages include, in addition to the local problems inherent in each machine, the basic ones that are presently present in most dough machines of continuous action, such as uneven mixing of the components of the formulation components at the first stage and the lack of qualitative plasticization of the dough in the third stage, also existing the problem is excessive heating of the dough with intense kneading of the dough [14–15].

Based on the theoretical researches and the obtained research results, after the comparative analysis of the working elements, there was decided to model the process of kneading the yeast wheat dough with the use of cam operating elements.

Materials and methods

Software simulation process

The mathematical modeling of the process of kneading wheat yeast dough by cam operating organs was carried out in the software complex GiPex 3D V17.

To simplify the mathematical description of the mechanical behavior of the dough for the corresponding parameters, the spatial averaging over the solid and gas phases was used.

Mathematical dependencies, geometric dimensions of the chamber, geometrical sizes of cam operating bodies, frequency of rotation, and experimental data obtained after a physical experiment were given to calculate and simulate the simulation of the process of mixing the yeast dough with cam operating organs into the GiPex 3D V17 software complex.

Structure of yeast dough

The dough is considered as a complex colloidal system, consisting of several continuous and periodic phases. Solids and liquids (gluten and water) in the dough are continuous phases, starch grains and gas formed during fermentation of the dough - a periodic phase. As a result, the physical properties of the dough are characterized by parameters of solids, liquids, gases and indicators resulting from the interaction of these phases. This process is carried out by mechanical processing of the dough, and consists in swelling of starch and protein complex with the formation of an elastic-elastic-viscous homogeneous mass containing active-active microorganisms and enzymes.

Simulation of the process of kneading yeast dough

The mathematical modeling of the process of mixing the yeast dough by cam operating elements was carried out with the help of the use of a modern software complex, in which the predicted equations of the movement of the yeast dough, the geometrical parameters of the chamber of kneading and cam working elements.

A mathematical model was selected for modeling the process of kneading wheat yeast dough, which is used to study the processes in which elastic, viscous and plastic deformations of dispersed, saturated materials occur during non-stationary regime of power load.

The area to which the ideology of the continuous medium can be applied will be called the characteristic volume, identifying with the proportion of the dough that is kneading. We will assume that the size of this element is much smaller than the sample size for research, and the entire volume can be typed from similar elements. To simplify the mathematical description of the mechanical behavior of the dough for the corresponding parameters we will use spatial averaging over the solid and gas phases.

Let us consider a certain characteristic volume V bounded by the surface Ω, occupied by a diphasic moving substance (Figure 2) [9-10].

That is, part of this volume V_1 is occupied by the first (solid-liquid) phase, and the second part of V_2 is the gas phase, ($V = V_1 + V_2$). Similarly, the part of the boundary surface Ω_1 belongs to the solid phase, and the other Ω_2 is the gas; $\Omega = \Omega_1 + \Omega_2$. Within the volume V there is (in the general case, a lot of bonds) the phase surface section Ωij (i, j = 1,2; i ≠ j). In the model description of the mechanical behavior of the disperse material in the process of force loading we use the hypothesis of its continuity within the equation of conservation of mass [10].

Mathematical dependencies, geometric dimensions of the chamber, geometrical sizes of cam operating elements, frequency of rotation, and experimental data obtained after a physical experiment were given to calculate and simulate the simulation of the process of mixing the yeast dough with cam operating elements.

At the stage of formation of the exercise, the conditions of the contact interaction of the material with the working elements and the chamber of mixing, as well as the values of the structural-mechanical characteristics of the dough (Table 1) are given.

To simulate the process, a calculated grid was used. The cam working elements rotated with a frequency of 60 rpm in the opposite direction and changed the angle by 45° (Figure 2). After the mechanical action by cam operation elements the share rate and dissipation were calculated via the software complex.

After entering into the software complex all the necessary parameters, the process of calculating and visualizing the process of mixing the yeast dough begins.

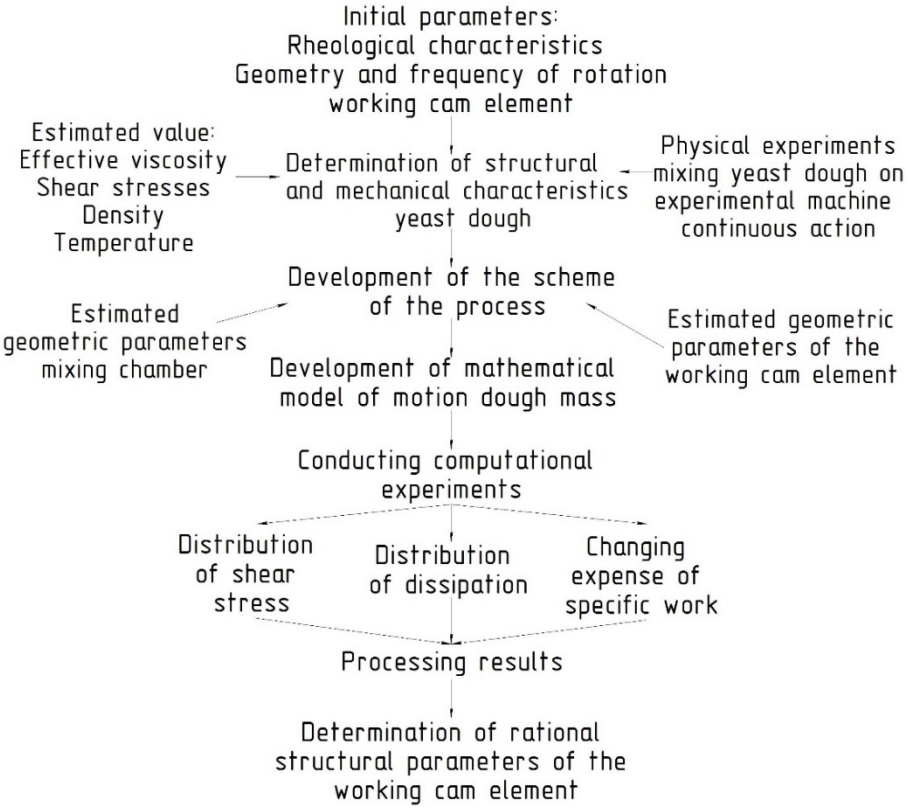


Figure 1. Scheme of simulation of the process of kneading yeast dough in a dough machine of continuous action

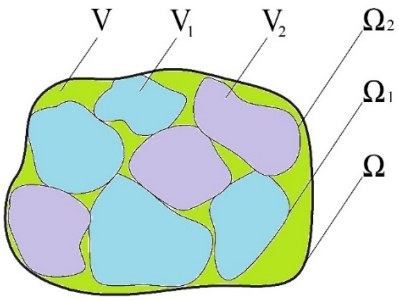
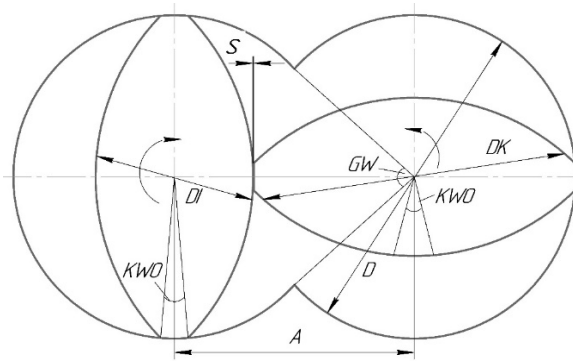


Figure 2. Characteristic volume V.
V_1 is the volume of the solid-liquid phase,
V_2 is the volume of the gas phase,
Ω_1 is the boundary surface of the solid-liquid phase,
Ω_2 is the boundary surface of gas phase

Output data before calculation the process of kneading wheat yeast dough



2D model **3D model**

Figure 3. Specified geometric dimensions mixing chamber and located therein cam working elements

Table 1

Output data before calculation the process of kneading wheat yeast dough by cam operating elements

Variable	Symbol	Calculation
Number of cams	Z	Given by the condition
The distance between the centers	A	Given by the condition
Diameter of the mixing chamber	D	Given by the condition
Step of the cams	T	Given by the condition
The gap between the top of the cam and the cylinder wall	Σ	Given by the condition
The gap between the cams	s	Given by the condition
The radius of the working chamber	RG	RG=D/2
Work camera angle	GW	GW=2 acos(A/D)
The outer diameter of the cam	DA	DA=DG - 2 s
The diameter of the core of the cam	DK	DK=2 A – DA – 2 s
The outer diameter of the cam	DE	DE=DA + s
The diameter of the core of the cam	DI	DI=2 A – DE
Angle of inclination, completely tangent	KW0	KW0=180°/Z-FW0
Angle of inclination, actual	FW1	FW1=180°/Z-(NW +KW1)/2
The width of the top, the actual	KB1	KB1=KW1/(2π)T
Marginal shear stress	G_0	$G_0=1{,}49\cdot10^{-4}$ MPa
Young's module	E	$E=9{,}2\cdot10^{-4}$ MPa
Poisson's coefficient	υ	υ=0,4
Effective dough viscosity	$\eta_{еф}$	$\eta = 3220\gamma^{-0,85}$
The initial temperature of the dough	t_0	t_0=30°C
Density of the dough	ρ	ρ=1400 kg/m^3
Rotation frequency WE	n	n=60 rpm

Results and discussion

Terms movement of the cam working element

Information technology design allows us to consider the technological process of mixing the yeast dough in the form of a system of interconnected objects of study (Figure 5)

Modeling of the process of mixing the yeast dough by the cam operating elements passes with a rotational speed of 60 rpm in a dual capacitive capacity. The cam's working elements turn to meet each other by kneading the yeast dough, moving the yeast dough in the crucible with the use of cam-like elements is depicted in Figure 4.

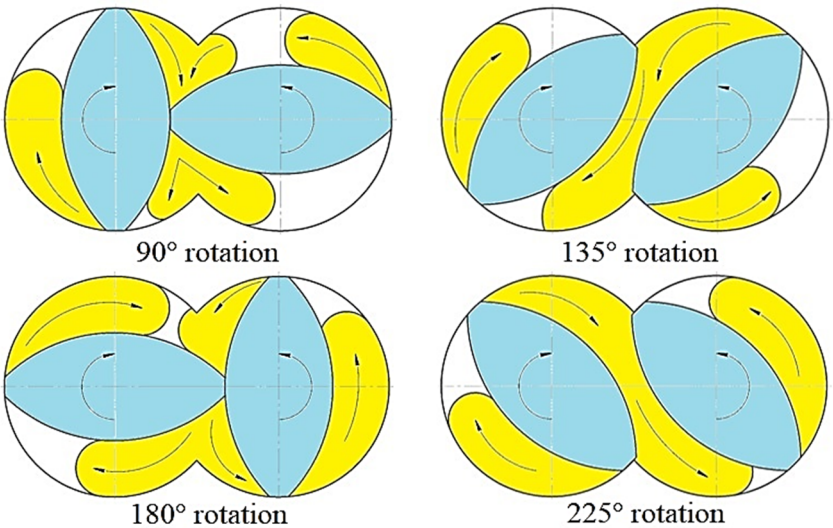


Figure 4. Moving the yeast dough in the crucible with the use of cam operating elements

Simulation of the process of mixing the yeast dough is needed for further calculation of the design, technological parameters and recommendations for the design of the working element and dough machine in general. Using simulation, we will determine the range of variation of the bias voltage and dissipation parameters. The purpose of which is to establish the rational value of the selected parameters in order to achieve the maximum effect from their effect on the process of kneading.

Design blocks of the kneading process

The initial data and boundary conditions were entered for simulation modeling of the process of mixing into the software complex, namely, to the calculation blocks (Figure 5): material properties, geometry and status of the process of mixing [11].

In the properties of the material, a two-component mixture with the properties of the pseudoplastic fluid was chosen. Geometric data are given in the geometry block and in the calculation parameters the counter-rotation of the cam's working bodies is selected. The mixing process status is selected as complete, not stable, alternating during mixing.

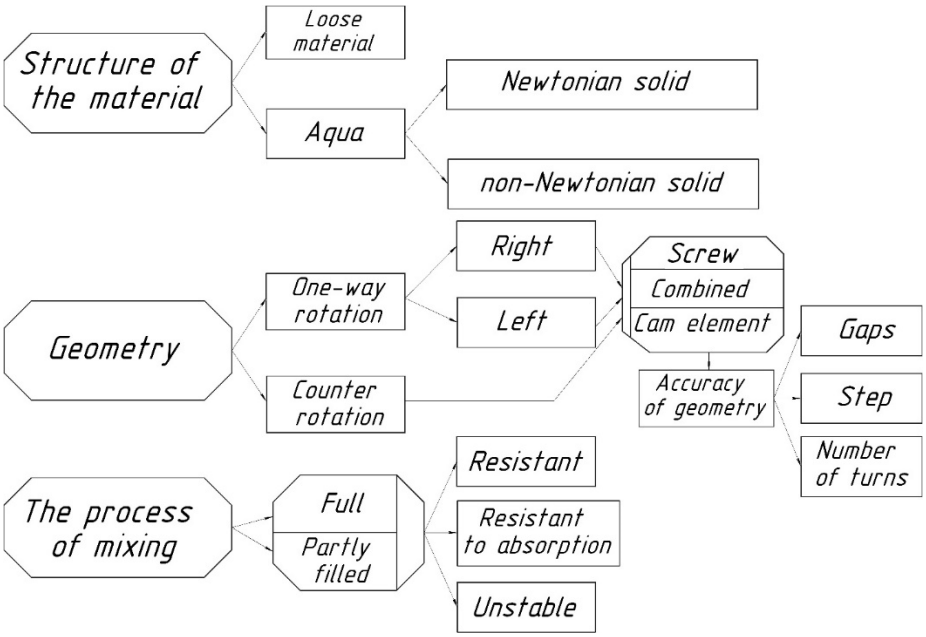


Figure 5. Scheme of imitative modeling of the process of mixing by cam operating elements

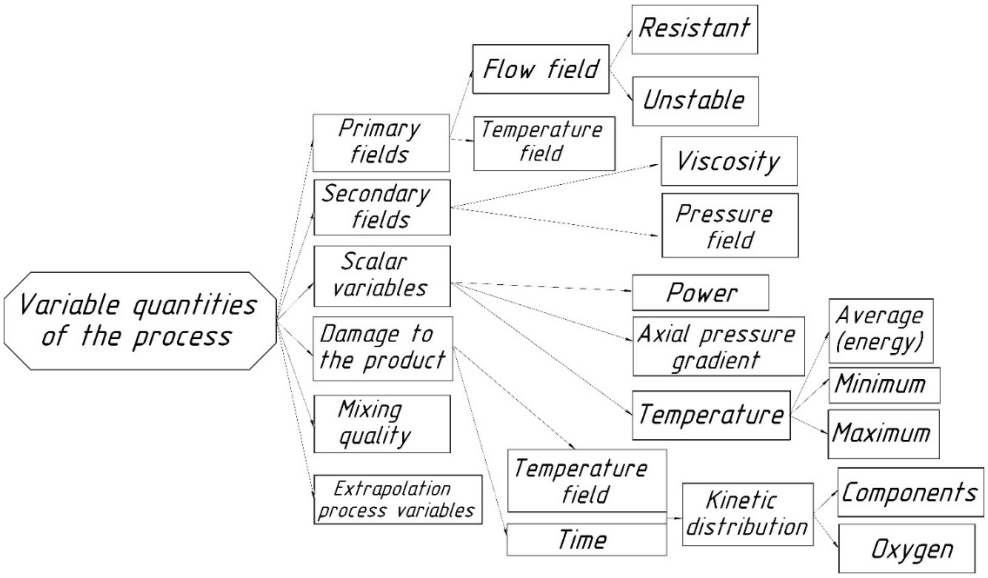


Figure 6. Depth of simulation modeling of the process of kneading by cam operating elements.

Using the depth of simulation (Figure 6) of the kneading process, we obtained a change in the shear stress and the distribution of dissipation in the crucible during the kneading of the yeast dough by cam operating elements.

Along with the characteristics of displacement and power, the mechanical characteristics of the voltage on the yeast dough are key features. The mechanical stress is characterized by the distribution of the shear stress on the yeast dough within the mixing chamber [8].

For pseudoplastic liquids with variable viscosity of a product (non-Newtonian fluid), the shear stress is of a power-law nature. Figure 6 shows the distribution of strain of displacement on the yeast dough during kneading by the cam operating elements and, as a result, the distribution of the mechanical load for a certain position of the cam operating elements.

Results

To study the shear stress, four basic positions of the cam's working elements were selected, then these provisions are repeated on the shaft of the working element.

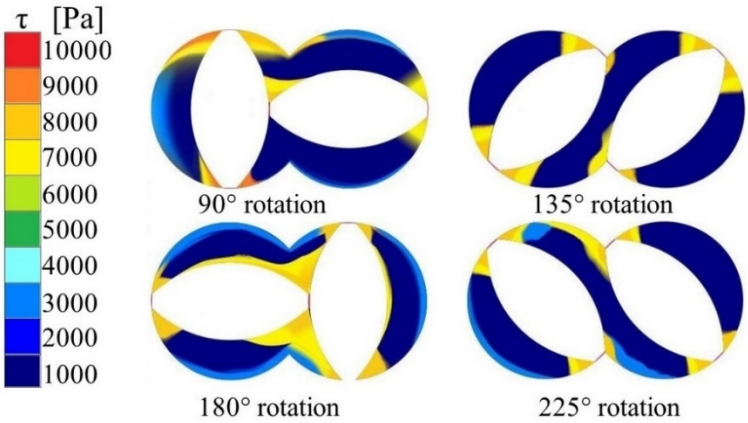


Figure 7. Change in the shear stress [τ, Pa] in the mist chamber in the process of mixing the yeast dough by the cam operating elements

On the greater part of the working volume there are not large indicators of shear stress (Figure 7). The greatest indices of shear strain during modeling of the process of mixing the yeast dough are observed in the field of interaction of the working element with the wall of the case and in the zone of engagement of the working elements. In the area of the engagement of the working elements and at the contact with the walls of the chamber, the shear stress values reach from 7000 to 8000 Pa. For the rest of the chamber, the displacement strain reaches 1000-3000 Pa.

The dissociation is proportional to the displacement velocity squared. Due to dissipation, the conversion of the kinetic energy of the stream into the heat occurs due to internal friction of the yeast dough with the working elements and the case [11].

The yeast dough is mixed in 12 pairs of cams, which are shifted at an angle of 45°, for the dissipation process it was decided to consider the process of kneading in the example of 3-6-9-12 pair of cams, since at the beginning of mixing there were noticeable changes in dissipation. By means of simulation, distribution of dissipation in the microscope was considered in the process of mixing the yeast dough with the cam operating elements (Figure 8).

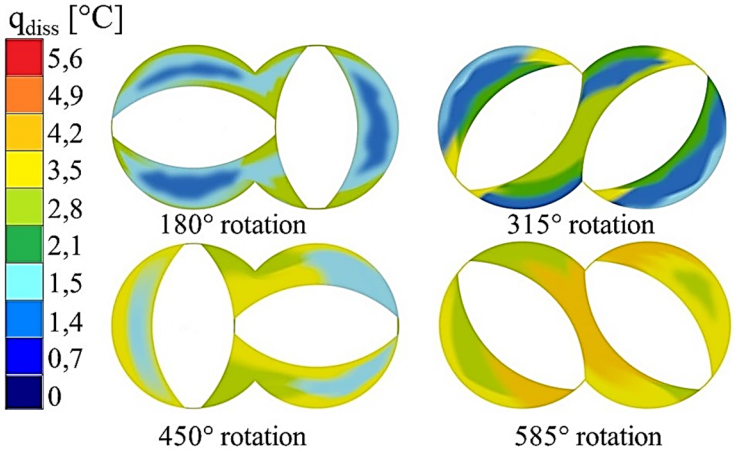


Figure 8. Distribution of dissipation [q_{diss}, ° C] in the chamber in the process of mixing the yeast dough by the cam working elements

Distribution of dissipation clearly shows in which parts of the working chamber is the formation of heat in the flow area. In the area of kneading 3 pairs of cam (180° rotation), there is no significant heat release, then during the mixing due to internal friction of the yeast dough with the working elements and the case there is an increase in the conversion of the kinetic energy of the stream into the heat and the temperature of the yeast dough increases. At the stamping site 12 pairs of cams, the temperature of the yeast dough increases by almost 5° C, thus taking into account that before the start of the simulation, the initial temperature was set to t = 30° C, then at the end of mixing, this temperature in the yeast dough reaches almost 35° C. The greatest amount of heat is observed in the sphere of cam involvement of the working elements.

Thus, the simulation parametric model of the process of mixing the yeast dough allowed to study in details the processes occurring in the mixing chamber of the dough, the dependence of the flow pattern on the design and configuration of the cam operating elements and the frequency of rotation [12].

The simulated parametric model of the process of mixing by cam operating elements, which allows to carry out design calculations effectively when choosing rational structural and technological parameters, is developed. Using the presented scientific and methodological developments will significantly accelerate and economically save the process of creating reliable process equipment for mixing yeast dough.

It is possible to rationalize the process of mixing the dough and reduce the time required for fumigation and fermentation by intensive mechanical processing of the dough by the cam operating elements and as a result of obtaining qualitative characteristics of the baking products.

It is advisable to mix the yeast dough with the use of the cam's working organs.

Checking the results on the physical model

Model verification for adequacy was carried out using an experimental dual-action machine of continuous action (Figure 9).

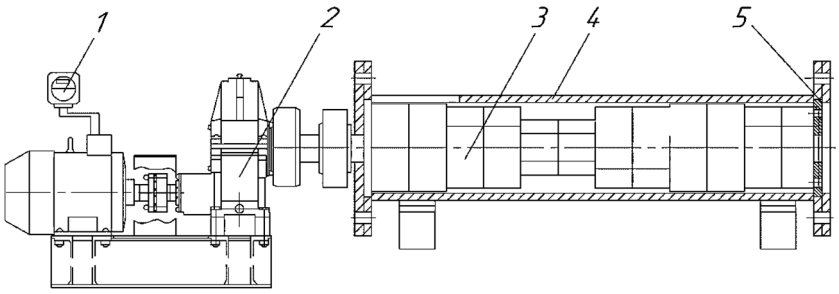


Figure 9. The scheme of an experimental installation with cam operating elements:
1 – a device for measuring electric power; 2 – drive; 3 – working element; 4 – frame;
5 – stabilizing grate.

The results of simulation of parametric modeling were tested on a physical model. Comparing the results (Figure 10-11) and performing mathematical processing, the error is less than 5%, the mathematical model corresponds to the adequacy.

The experimental installation works as follows, the raw material enters the receiving hopper, after which, using the working bodies and their influence, the process of kneading is carried out, after which the dough comes out through the stabilizing grill.

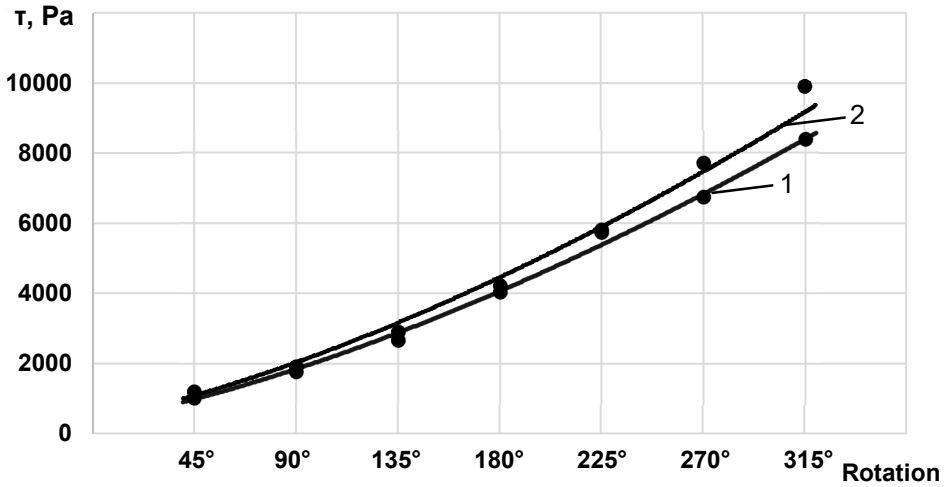


Figure 10. Comparison of the results of the physical and mathematical modeling of the displacement stress [τ, Pa] in the mixing chamber at different angles of rotation of the cam element (1-imitation, 2 - physical)

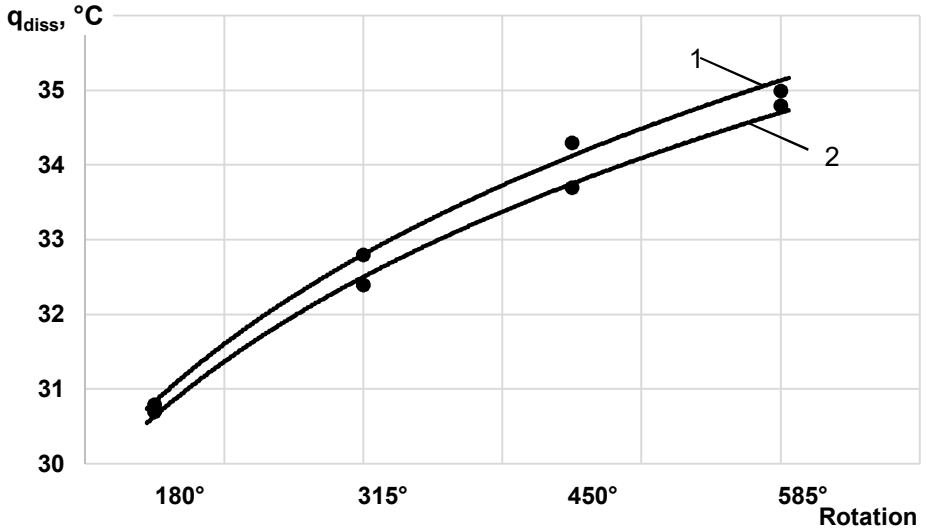


Figure 11. Comparison of the results of the physical and mathematical modeling of the distribution of dissipation [q_{diss}, °C] in the mixing chamber at different angles of rotation of the cam element (1-physical, 2-simulation)

The results of the computational experiments allowed to investigate the process of mixing the yeast dough by the cam operating elements in the stirring chamber. By means of simulation, the change in the stresses of the shift of the yeast dough in the stirring chamber was investigated, the distribution of dissipation in the chamber of stirring and the temperature change during the kneading process were investigated. It is determined that for a rotational speed of a working element of 60 rpm, the temperature of the yeast dough rises to 5°C, which is admissible while kneading the dough. The obtained simulation results will be used to organize the technological process and design new equipment for mixing the yeast dough.

Conclusions

It was investigated the change of the stresses of the shift of the yeast dough in the stirring chamber, in the region of the contact between the working elements and at the contact with the walls of the chamber, the shear stresses reach from 7000 to 8000 Pa, and the rest of the shrinkage chamber displaces a strain of 1000-3000 Pa. The distribution of dissipation in the chamber of stirring and the temperature change during the mixing process was investigated, and the temperature of the yeast dough was raised to 5°C for the rotation of the working element 60 rpm, which is admissible when kneading the dough.

On the basis of simulation modeling of the process of mixing the yeast dough, effective working elements are proposed for mixing the yeast dough in a dough machine of continuous action.

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Impact of the insurance costs on the competitiveness of food industry enterprises of Ukraine in the context of the food market security

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Abstract

Introduction. The study was carried out to analyze insurance costs and to determine the trends, patterns and impact of the insurance costs on the competitiveness of food industry enterprises in the context of the food market security.

Materials and methods. The theoretical background of the article is based on critical literature review of the insurance costs, food market security and competitiveness. It were used the methods of comparative, statistical analysis of data, systematization, scientific interpretation; generalizations and comparisons the indicators of market share and capacity, profitability and efficiency, insurance costs and correlation-regression analysis methods and indicators.

Results and discussion. The investigated FIEs do not violate the norms of the current antimonopoly legislation of Ukraine. The highest values of all three types of profitability were related to the PJSC "Karlsberg Ukraine". It was determined the rates of change in insurance costs for the selected list of food industry enterprises. The results shows wide range of values from -99.6 % (PJSC "The house of vintage cognacs "Tauria"), to 881.4 % (PJSC "Pologovsky Oil Extraction Plant") in 2014-2015. The research results show that the largest share of insurance costs related to the PJSC "Pologovsky Oil Extraction Plant" in 2016 and equal to 2.173%. Consequently, the cost of insurance insignificantly changes the production costs and, accordingly, moderately affect the formation of profits for FIEs.

The analysis shows a direct proportional relationship between *ROE* and insurance costs for PJSC "Karlsberg Ukraine", and the inverse proportionality between *ROS* and insurance costs for PJSC "Obolon" and Private JSC "Kyiv Confectionary Factory "Roshen".The correlation-regression analysis of profitability and insurance costs for FIEs shows that only three coefficients of determination correspond to the value of a regressive model of satisfactory quality: r^2=0.717 (*ROE*, PJSC "Karlsberg Ukraine"); r^2=0.838 (*ROS*, PJSC "Obolon"); r^2=0.664 (*ROS*, Private JSC "Kyiv Confectionary Factory "Roshen"). The lower values (the interval r^2 for 0.1-0.5) of the determination coefficient are fixed in nine cases: within the limits of the minimum value r^2=0.103 for *ROS* to the PJSC "Pologovsky Oil Extraction Plant", and to the maximum r^2=0.496 for *ROE* to the PJSC "Kyivkhlib.

Conclusions. The hypothesis about the existence of a dependence between the competitiveness of FIEs and the portion of money allocated to FIEs for insurance is confirmed only for FIEs with high efficiency of doing business.

Introduction

The food industry is the leading industry in the agro-industrial complex of Ukraine, as evidenced by data on consumption volumes of its products in the markets [23, 29]. At the same time, food industry enterprises (further referred to as FIEs), which, like most industrial enterprises, may be exposed to risks that could significantly impair financial performance [26-29]. From these positions, the appropriateness of insurance becomes evident, as it serves as a necessary and effective tool for protecting against risks and contributes to increasing the competitiveness of the enterprise [38]. In addition, it should also be noted that the current trends in international experience in the functioning of agro-industrial enterprises (including FIEs) in agricultural sector (ACS), show the important role of insurance as an element of security in the food market [45-47]. The nature of such interaction will be investigated in the presented study.

Issues of the impact of insurance and the effectiveness of the FIEs and ACS are discussed by different foreign researchers. *Akinrinola O.O.* and *Okunola A.M. (2014)* have studied the effect of agricultural insurance scheme on agricultural production in Ondo state (Nigeria). Scientists have determined that there may be an increase in the level of investment of farms after participating in insurance. This is due to the availability of agricultural loans secured by insurance coverage. Farmers also increased the size of their farms and output volumes [1]. *Spörri M., Baráth L., Bokusheva R. and Fertö I.(2012)* have investigated the impact of crop insurance on the productivity of Hungarian farms and revealed the negative impact of insurance on economic indicators of economic profit, productivity of labor and productivity of land [2].

Juan H. et al.(2016) proposed a theoretical model that counts several features of the insurance program of the crop, taking into account the empirical parameter of interest. The model also forecasts the condition of positive impact of insurance on the use of enterprise resources, if preliminary estimation of efficiency will be carried out [3].

Also, special attention among foreign studies deserves the following researchers: *Zhao Y.* and *Preckel P. (2016)* with an empirical analysis of the effect of crop insurance on farmers' income" [4]; *Kim Y., Pendell D.L.* and *Yu J. (2018)* with effects of crop insurance on farm disinvestment and exit decisions [5]; *Jisang Yua J.* and *Sumnerb D.A. (2017)* with effects of subsidized crop insurance on crop choices [6]; *Bachev H. (2012)* with risk management in the ACS [7]; *Lorant A.* and *Farkas M.F. (2015)* with risk management in the ACS with special attention to insurance [8] and many others.

Most of Ukrainian researchers assess the competitiveness of the national FIEs and ACS of Ukraine without taking into account insurance. *Baeva V.V. (2015.)* notes that at present there is no generally accepted method for assessing competitiveness, but all methodological approaches can be divided into quantitative and qualitative ones [9].

According to *Pylypenko V.V. and Pylypenko N.M. (2016)* there exist three groups of activity characteristics: agricultural enterprise (product competitiveness, market environment and financial and economic status) and one needs expert judgment for weighting factors to evaluate effective competition [10].

Legeza D.G. (2011) focuses on methods of assessing the competitiveness of agricultural products through twelve indicators, including the proportion of material costs, merchantability, profit, profitability, etc. [11].

Cherednichenko O.O. (2013.) investigates the evaluation of the competitiveness of dairy agricultural enterprises on the basis of three approaches: 1) the traditional method of assessing the competitiveness of goods by calculating unit and group indicators; 2) marketing approach taking into account the consumer's requirements for price and quality of goods and

factors that determine the competitiveness of all marketing activities of the enterprise; 3) production approach, based on the assessment of the profitability of sales of a particular product and its market share [12].

Tycholyz L.S. (2013.) generalizes methods of assessing the competitiveness of agricultural enterprises in nine groups [13].

The analysis of the development of the FIEs of Ukraine is the object of research of many Ukrainian scientists from different positions as follow below.

Irytytsheva I.O. (2012) pays attention on the necessity of developing a qualitative plan [14], *Vasilchenko K.G. (2013)* defines the prospects of innovation in the food industry [5], *Kvasko A.V. (2017)* notes that the problem of choosing a universal indicator and factors of competitiveness remains unresolved [16], *Buracek I.V.* and *Bilenchuk O.O. (2016)* analyze the competitiveness of the enterprise competitiveness of the subject of economic activity [17], *Shwed T.V* and *Bila I.S. (2017)* group methods of assessing the competitiveness of enterprises [18]. As far as we know, the analysis of the impact of the cost of insurance on the competitiveness of FIEs is still beyond the attention of researchers. This gap is under the attention in presented study.

Our investigation is also related to the food market security. *Isaboke et al. (2016)* described the effect of weather index based micro-insurance on food security status of smallholders, and find that a positive impact on food security is associated with the uptake of index insurance [45]. *Mârzaa et al. (2015)* suggest that insurance alone cannot provide food security. It can make a big impact in raising awareness of the importance of risk reducing and encouraging investments in increasing the ACS development 46]. According to the report of the *Agricultural Insurance Conference (Berlin, 2014)* agricultural insurance should be seen as one component of the ACS and it is related to food security [47].

We aim to analyze insurance costs, performance indicators and competitiveness of food industry enterprises in Ukraine and to identify trends and patterns that may exist on the market and relationships between insurance costs, competitiveness of the FIEs and food market security.

To achieve this goal it is necessary to accomplish the following tasks:

- to systematize data about the cost of insurance for FIEs through financial reporting, official private and public Internet resources;
- promote and test hypotheses regarding the interaction link between competitiveness of the FIEs and amount of money allocated for insurance, and validate the hypotheses regarding the FIEs propensity to insurance with a higher competitiveness.

Materials and methods

Materials. The theoretical background of the article is based on competitiveness theories explaining the ability of the market subjects to act on a par with competitors that present there [19-20]. The information base of the study was financial reporting, private and official public Internet resources, information from the official website of the Agency for the Development of the Stock Market Infrastructure of Ukraine [21] and State Statistics Service of Ukraine [22]. In order to create a database of insurance companies' expenses for the years 2013-2017, data from more than 500 FIEs of Ukraine was analyzed, however, reliable information was collected about only 13 FIEs. The search for FIEs was carried out according to the code of the Unified State Register of Enterprises and Organizations of Ukraine [49-50].

Methods. With the aim to determine the trends, patterns and impact of the insurance costs on the competitiveness of food industry enterprises in the context of the food market security, we implemented the critical literature review, content, comparative [1-5], statistical analysis of data [6-9, 11], systematization and synthesis [12, 14-18], scientific interpretation and scientific discourse analysis methods [24-31]. Systematization and critical literature review methods were used to prepare a theoretical background for our research study [1-18, 20-49].

The methods of comparative and statistical analysis of data was used in the study of data from the Agency for the Development of the Stock Market Infrastructure of Ukraine [21] and from the State Statistics Service of Ukraine [22]. During the processing such data, it turned out that information on insurance costs for FIEs is not provided or such information is provided only for few years of the proposed study period 2013-2017. Due to the data of Agency for the Development of the Stock Market Infrastructure of Ukraine, we have determined the insurance costs for each year in the find tab "Notes to the Financial Statements, prepared in accordance with international financial reporting standards" [21-22]. In most cases that indicator is designated as "Insurance" or "Insurance costs", etc.

The results of the studies the impact of the insurance costs on the competitiveness of food industry enterprises in the context of the food market security are obtained through the use of grouping methods [1-3], generalizations and comparisons the indicators of market share and capacity [8, 10], profitability and efficiency, insurance costs and correlation-regression analysis methods and indicators [4-17].

Results and discussion

Considering the competitiveness of FIEs as a factor in successful business development, it is necessary to determine the definitions. We consider the definition of "competitiveness" as a complex comparative characteristic, which determines the degree of advantage of a set of indices of one FIE over the aggregate of other FIEs indicators and characterizes the ability to compete. The competitiveness of FIEs is achieved in the presence of rivalry in order to expand and win the market in the struggle for the consumer, for the sake of victory of competitors and profits [19]. The assessment of FIEs competitiveness can be achieved by comparing various aspects and the most significant indicators of FIEs activity, including indicators such as performance, market share, concentration, etc.

It is also worth noting that insurance for FIEs as a prerequisite for ensuring competitiveness, also contributes to ensuring security in the food market.

According the approach by *Porter M.*, "competitiveness" of the market subjects relations – it is his ability to act on a par with competitors that present there [20]. Consequently, in order to assess competitiveness, it is necessary to identify competitors, collect the information about market capacities and benefits.

The general factors that determine the competitiveness of FIEs and the needs of food products industry, researchers traditionally include: the size of cash incomes, the volume and range of food products, the level of saturation of the market by certain types of products, the level of retail prices for goods; the number and age structure of the population, its national habits, the level of trade organization [15]. The list below does not cover FIEs expenses for insurance. That is why, according to this research, we are starting a new direction of research and will carry out an analysis of insurance costs, indicators of efficiency and competitiveness of the FIEs of Ukraine.

Our scientific *first hypothesis* is formulated as follows: "*the main subjects of the food industry market with a higher competitiveness are more prone to insurance*". The *second hypothesis* is as follows: "*there is a relationship between the competitiveness of the FIEs and the portion of the money allocated to the insurance business*".

Market share and capacity

For completeness of the description of selected FIEs, we will investigate the contributions of such FIEs to the food industry of Ukraine and the level of influence on the formation of gross domestic product (GDP) during 2013-2017. For further analysis, we propose the indicators of concentration and capacity of the enterprise.

An analysis of the situation of the company in the market is calculated by using a specific share of the entity, which we defined as net income (NI) from the main operating activity:

$$C_1 = 100\% \, NI_1 / NI, \quad (1)$$

where C_1 – shares of the entity in the net income of all enterprises in the market (in %), NI_1 – net income of enterprise (UAH), NI – net income of all enterprises in the market (in our case, the total net income on the food industry market of Ukraine). Net income of enterprise (NI_1) is determined by the line 2000 form 2 of the report on the financial results of the FIEs and determines the net proceeds from the sale.

To determine the degree of monopolization in the market use the so-called concentration factor *CR*, which is determined by adding the shares of individual players: for example, $CR_2=K_1+K_2$ for the first two market subjects, CR_3 for the first three market subjects etc., which are the most successful market participants. The current antimonopoly legislation of Ukraine defines the criteria for monopolization of the market when: $CR_1>35\%$; $CR_3>50\%$; $CR_5>70\%$ [19].

The next indicator will be the capacity (η) of the enterprise, which we determine with the share of net income of the enterprise in the formation of GDP of Ukraine by the formula:

$$\eta_1 = 100\% \, NI_1 / GDP. \quad (2)$$

where η_1 – capacity of one enterprise in percent, GDP – the value of the gross domestic product of Ukraine (UAH).

As we can see, the investigated FIEs do not violate the norms of the current antimonopoly legislation of Ukraine.

Based on the data of the table 1, it has been determined that among the list of enterprises represented the largest share in both the food industry and GDP of Ukraine is related to the PJSC "Karlsberg Ukraine", the average arithmetic mean of the corresponding values of the share for the study period 2013-2017 is equal to 1.173 % and 0.220 %. At the same time, the smallest similar values are characteristic for PJSC "Sumy food products factory" – 0.028 % and 0.005 %.

We will examine the following indicators for sample enterprises (table 1).

Table 1

Indicators of the share and capacity of the FIEs

Enterprise	Indicators K_1 and η_1	Values of indexes by years, %				
		2013	2014	2015	2016	2017
PJSC "Karlsberg Ukraine"	K_1	1.371	1.145	1.151	1.103	1.096
	η_1	0.237	0.218	0.230	0.214	0.202
PJSC "Obolon"	K_1	1.530	1.055	0.915	0.762	0.905
	η_1	0.265	0.201	0.183	0.148	0.166
PJSC "Kyivkhlib"	K_1	0.744	0.560	0.493	0.601	0.415
	η_1	0.129	0.107	0.099	0.116	0.076
PJSC "Pologovsky Oil Extraction Plant"	K_1	0.440	0.535	0.669	0.535	0.568
	η_1	0.076	0.102	0.134	0.104	0.104
Private JSC "APK-INVEST"	K_1	0.396	0.455	0.464	0.418	0.486
	η_1	0.069	0.087	0.093	0.081	0.089
PJSC "Zhytomyr Butter Factory"	K_1	0.396	0.392	0.384	0.384	0.355
	η_1	0.068	0.075	0.077	0.074	0.065
PJSC "Kharkiv Biscuit Factory"	K_1	0.342	0.338	0.396	0.403	0.369
	η_1	0.059	0.064	0.079	0.078	0.068
PJSC "Dniprovsky starch flour combine"	K_1	0.149	0.146	0.156	0.117	0.139
	η_1	0.026	0.028	0.031	0.023	0.025
Private JSC "Kyiv Confectionary Factory "Roshen"	K_1	0.196	0.097	0.063	0.050	0.047
	η_1	0.034	0.019	0.013	0.010	0.009
PJSC "The house of vintage cognacs "Tauria"	K_1	0.076	0.150	0.181	0.152	0.141
	η_1	0.013	0.029	0.036	0.030	0.026
PJSC "Confectionery Factory "Kharkivyanka"	K_1	0.066	0.062	0.046	0.050	0.057
	η_1	0.011	0.012	0.009	0.010	0.010
PJSC "Kremenchug confectionery factory"	K_1	0.062	0.040	0.045	0.040	0.040
	η_1	0.011	0.008	0.009	0.008	0.007
PJSC "Sumy food products factory"	K_1	0.003	0.031	0.038	0.032	0.034
	η_1	0.001	0.006	0.008	0.006	0.006

* Author's calculations based on official data [21; 22].

Profitability and efficiency

Speaking about the effectiveness of the FIEs, it should be noted that efficiency characterizes economic results for each unit cost. The most commonly used measure of effectiveness is ROA (return on assets), which is determined by the formula:

$$ROA = 100\% \text{ NP} / \text{A}. \quad (3)$$

where NP – net profit of the FIEs. Net profit is a net financial result: the profit determined by line 2350 for a positive result and line 2355 for the event of losses.

The efficiency of FIEs is provided under the following conditions:

$$ROA \rightarrow \max, ROA > 0.$$

Another indicator of efficiency can be the rate of return on equity *ROE* (return on equity), which we define by the formula:

$$ROE = 100\% \text{ NP} / \text{E}. \quad (4)$$

The value of E is equity, which is determined by line 1495 of form 1 of the balance sheet of the financial statements of the enterprise.

Under the following conditions: $ROE > 10\%$, investments can be considered successful.

It is also worth considering the ROS (return on sales) profitability based on net income:

$$ROS = 100\% \text{ NP} / \text{NI}_1. \quad (5)$$

where *ROS* – return on sales, NI_1 – income of the sales.

Let's move on to assess the effectiveness of the FIEs according to the profitability indicators (table 2).

During the study period 2013-2017, among the selected list of food industry enterprises, the highest values of all three types of profitability were related to the PJSC "Karlsberg Ukraine". At the same time, for many investigated enterprises (PJSC "Obolon", PJSC "Kyivkhlib", PJSC "Sumy food products factory", PJSC "Pologovsky Oil Extraction Plant" and PJSC "Kremenchug confectionery factory") these indicators for individual periods could be regarded as indicators of loss.

The low value of the profitability of the FIEs in Ukraine the researchers explain by the problems of the industry itself, as well as the economic and political situation in the country [14; 23; 24]. In order to improve the situation and increase the competitiveness of the FIEs, various measures are proposed, among which: the use of advanced production technologies; improvement of the qualification base of employees; improvement of the infrastructure of storage and distribution of products of food producers; strengthening of quality control and product safety [25].

Table 2

Profitability indicators of the FIEs in Ukraine*

Enterprise	Indicators	Calculated values of profitability by years, %				
		2013	2014	2015	2016	2017
PJSC "Karlsberg Ukraine"	*ROA*	17.05	21.05	20.49	18.78	20.72
	ROE	21.17	26.71	27.28	30.03	35.77
	ROS	45.49	42.03	36.13	40.67	42.12
PJSC "Obolon"	*ROA*	5.38	–18.30	–12.54	–4.65	2.61
	ROE	16.10	–74.40	-159.32	–26.73	7.34
	ROS	38.04	36.40	34.42	32.51	28.17
PJSC "Kyivkhlib"	*ROA*	5.88	–5.07	–5.38	2.88	1.96
	ROE	14.37	–11.70	–20.13	13.55	9.58
	ROS	23.02	24.27	26.94	24.92	24.25
PJSC "Pologovsky Oil Extraction Plant"	*ROA*	3.56	–1.38	12.90	–1.22	0.99
	ROE	13.91	–4.42	38.84	–4.24	4.32
	ROS	12.17	25.18	16.88	13.07	9.46
Private JSC "APK–INVEST"	*ROA*	6.54	–3.72	2.17	6.60	18.56
	ROE	33.80	–19.65	10.39	17.21	33.58
	ROS	17.64	–7.48	3.54	13.07	33.37
PJSC "Zhytomyr Butter Factory"	*ROA*	10.00	13.20	14.71	16.88	10.94
	ROE	12.97	16.47	18.23	21.41	16.27
	ROS	25.63	24.03	24.03	25.25	26.06
PJSC "Kharkiv Biscuit Factory"	*ROA*	6.55	20.89	19.96	12.57	13.45
	ROE	7.33	22.37	22.01	13.91	14.83
	ROS	14.78	17.81	15.06	13.34	14.72
PJSC "Dniprovsky starch flour combine"	*ROA*	1.97	0.37	4.59	–1.07	2.41
	ROE	3.17	0.66	8.78	–2.55	8.06
	ROS	3.18	0.58	5.82	–2.00	4.62
Private JSC "Kyiv Confectionary Factory "Roshen"	*ROA*	0.47	4.35	1.48	0.57	0.38
	ROE	0.81	6.94	2.10	0.74	0.52
	ROS	8.37	12.97	13.85	12.08	11.88
PJSC "The house of vintage cognacs "Tauria"	*ROA*	0.23	–6.01	17.01	3.61	1.42
	ROE	0.53	–16.08	47.96	14.45	5.75
	ROS	72.66	47.20	51.57	19.25	14.37
PJSC "Confectionery Factory "Kharkivyanka"	*ROA*	1.26	3.38	2.09	1.94	8.23
	ROE	1.99	5.14	4.44	5.08	19.66
	ROS	1.30	3.13	2.88	2.75	9.03
PJSC "Kremenchug confectionery factory"	*ROA*	–1.29	–2.86	0.92	–0.19	0.00
	ROE	–3.01	–6.18	2.60	–0.81	0.01
	ROS	10.40	6.08	10.60	8.63	8.95
PJSC "Sumy food products factory"	*ROA*	–4.26	7.00	–14.43	0.18	0.95
	ROE	–6.66	15.83	–38.74	0.32	1.91
	ROS	11.59	8.45	3.83	4.01	8.34

* Author's calculations based on official data [21].

Insurance costs

The research of the FIEs and theirs insurance costs (IC_1) was conducted for checking of the first hypothesis of our research (table 3).

Data of the Table 3 characterize the dynamics of insurance costs for the FIEs of Ukraine. It should be noted that, in accordance with the conditions for the presentation of this information in the financial statements of the entities presented, one can distinguish the following features:

- Firstly, some companies data on insurance costs separate the individual components and indicate it in the reporting: PJSC "Kyivkhlib" (two types: the cost of property insurance and insurance costs are included in "Expenses on sales");
- Secondly, two out of the thirteen investigated companies made public health insurance data for their employees PJSC "Kremenchug confectionery factory" and Private JSC "Kyiv Confectionary Factory "Roshen").

Table 3

Insurance costs for food industry enterprises in Ukraine*

Name of the FIE	Insurance costs, thousand UAH				
	2013	2014	2015	2016	2017
PJSC "Karlsberg Ukraine"	6142	6190	7279	10248	10231
PJSC "Obolon"	2055	1902	2188	2210	2528
PJSC "Kyivkhlib"	241	341	340	122	319
PJSC "Pologovsky Oil Extraction Plant"	4798.5	3799.8	37290.2	46738	20863
Private JSC "APK-INVEST"	1151.8	1639.7	2200.1	2441.7	2283.4
PJSC "Zhytomyr Butter Factory"	385	305	593	547	677
PJSC "Kharkiv Biscuit Factory"	182	160	206	185	224
PJSC "Dniprovsky starch flour combine"	no data	no data	456	930	1055
Private JSC "Kyiv Confectionary Factory "Roshen"	2071	1250	589	582	677
PJSC "The house of vintage cognacs "Tauria"	298	267	47	292	54
PJSC "Confectionery Factory "Kharkivyanka"	no data	69	79	61	70
PJSC "Kremenchug confectionery factory"	1199	655	347	391	391
PJSC "Sumy food products factory"	38	61	45	45	73

* Author's calculations based on official data [21].

For a more detailed study of the cost of insurance, we will analyze the rate of their change in percentage over the years 2013-2017. The rate of change in insurance costs for the selected FIEs list shows results in a wide range of values: from -99.6 % (PJSC "The house of vintage cognacs "Tauria"), to 881.4 % (PJSC "Pologovsky Oil Extraction Plant") in 2014-2015. In this case, the calculated average arithmetic values of the rate of change in insurance costs during 2013-2017 years ranged from – 27.4% (PJSC "The house of vintage cognacs "Tauria", property insurance costs in other operating costs) and to 207.6% (PJSC "Pologovsky Oil Extraction Plant").

Insurance costs are an integral part of the entity's total costs, and therefore it would be expedient to analyze their share in total costs by the formula:

$$S_I = 100\% \, IC_1 / PC_1. \quad (6)$$

where S_I – share of insurance costs in total costs, IC_1 – insurance costs, PC_1 – production costs (costs of sold products). Insurance costs IC_1 is determined in accordance with the notes to the financial statements, which was prepared in accordance with international financial reporting standards; the value of PC_1 is determined by line 2050 forms 2 financial statements of the enterprise.

It is noteworthy that the cost of production shows the costs of preparation for production, marketing of products (direct material costs, direct labor costs, other direct costs, variable generic and permanent distributed production costs, etc.). Therefore, cost is the best indicator for determining the cost of an enterprise, but the list and composition of articles of cost is determined by the enterprise itself.

The relative share of the insurance costs in the cost of the selected for the study of FIEs of Ukraine is characterized by quite different values (table 4).

Among the selected list of food industry enterprises in Ukraine the largest insurance costs compared with production cost are related to the PJSC "Pologovsky Oil Extraction Plant", the maximum share of which insurance costs is 2.173% in 2016, thus in 2013-2017 the average value of this indicator is 1.08 % of total production costs. The smallest values of the share of insurance costs in the total production costs per study period of 2013-2017 years are related to the PJSC "Kyivkhlib": from 0.007 % in 2016, and to 0.027 % in 2014.

In general, there is a small impact of the insurance cost on the total production costs of FIEs. The largest share of insurance costs related to the PJSC "Pologovsky Oil Extraction Plant" in 2016 and equal to 2.173%. Consequently, the cost of insurance insignificantly changes the production costs and, accordingly, moderately affect the formation of profits for FIEs.

In the first place, the share of insurance costs in total production costs are PJSC "Pologovsky Oil Extraction Plant", PJSC "Karlsberg Ukraine", Private JSC "Kyiv Confectionary Factory "Roshen". These enterprises also have high profitability and efficiency, but there are others in the list in Table 2. Thus, the analysis does not fully support the first hypothesis that "the main subjects of the food industry market with a higher competitiveness are more prone to insurance".

Table 4

Share of insurance costs in the cost of sold products of the FIEs of Ukraine*

Name of the FIE	Percentage of insurance costs, %				
	2013	2014	2015	2016	2017
PJSC "Karlsberg Ukraine"	0.324	0.308	0.249	0.339	0.294
PJSC "Obolon"	0.114	0.094	0.092	0.093	0.071
PJSC "Kyivkhlib"	0.017	0.027	0.024	0.007	0.016
PJSC "Pologovsky Oil Extraction Plant"	0.489	0.314	1.684	2.173	0.740
Private JSC "APK-INVEST"	0.121	0.134	0.139	0.149	0.101
PJSC "Zhytomyr Butter Factory"	0.052	0.034	0.051	0.041	0.047
PJSC "Kharkiv Biscuit Factory"	0.025	0.019	0.015	0.011	0.013
PJSC "Dniprovsky starch flour combine"	no data	no data	0.093	0.192	0.173
Private JSC "Kyiv Confectionary Factory "Roshen"	0.451	0.488	0.273	0.285	0.296
PJSC "The house of vintage cognacs "Tauria"	0.563	0.111	0.013	0.051	0.008
PJSC "Confectionery Factory "Kharkivyanka"	no data	0.040	0.048	0.030	0.025
PJSC "Kremenchug confectionery factory"	0.851	0.582	0.216	0.233	0.197
PJSC "Sumy food products factory"	0.044	0.828	0.031	0.032	0.043

* Author's calculations based on official data [21].

Correlation-regression analysis

To test the hypotheses, we will investigate the insurance cost impact on performance and competitiveness of the FIEs. The hypothesis test was performed using a one-factor regression model. This is done by an argument variable X for insurance costs IC_1 (table 3), but the target function of the analysis (dependent variable Y) – profitability indicators *ROA, ROE, ROS* (table 1). Equation of pair linear regression was constructed in the form of dependence Y=A+BX. The corresponding calculations are given in Table 5.

Table 5

Indicators of correlation-regression analysis of profitability (Y) and insurance costs (X) for FIEs of Ukraine for 2013-2017*

Name of the FIE	Y	Regression equation Y = A + B X, %	r	t	r^2
PJSC "Karlsberg Ukraine"	*ROA*	18.63163 + 0.00012 X	0.152	0.266	0.023
	ROE	10.82388 + 0.00217 X	0.846	2.754	0.717
	ROS	43.59190 – 0.00029 X	–0.176	–0.310	0.031
PJSC "Obolon"	*ROA*	–56.03494 + 0.02322 X	0.539	1.109	0.291
	ROE	-233.16845 + 0.08535 X	0.275	0.495	0.076
	ROS	66.76113 – 0.01509 X	–0.915	–3.940	0.838
PJSC "Kyivkhlib"	*ROA*	9.68156 – 0.03532 X	–0.657	–1.509	0.431
	ROE	33.85275 – 0.12002 X	–0.704	–1.719	0.496
	ROS	23.74181 + 0.00344 X	0.224	0.398	0.050
PJSC "Pologovsky Oil Extraction Plant"	*ROA*	1.12776 + 0.00008 X	0.264	0.474	0.070
	ROE	5.18705 + 0.00020 X	0.212	0.375	0.045
	ROS	17.67346 – 0.00010 X	–0.321	–0.588	0.103
Private JSC "APK–INVEST"	*ROA*	–4.30831 + 0.00532 X	0.349	0.644	0.122
	ROE	11.89179 + 0.00163 X	0.040	0.069	0.002
	ROS	0.05195 + 0.00616 X	0.215	0.382	0.046
PJSC "Zhytomyr Butter Factory"	*ROA*	11.63393 + 0.00302 X	0.165	0.290	0.027
	ROE	12.99793 + 0.00812 X	0.403	0.762	0.162
	ROS	23.78787 + 0.00242 X	0.397	0.749	0.158
PJSC "Kharkiv Biscuit Factory"	*ROA*	20.13320 – 0.02847 X	–0.118	–0.206	0.014
	ROE	20.53562 – 0.02323 X	–0.090	–0.157	0.008
	ROS	21.84916 – 0.03504 X	–0.524	–1.066	0.275
PJSC "Dniprovsky starch flour combine"	*ROA*	6.80305 – 0.00593 X	–0.657	–0.870	0.431
	ROE	10.84164 – 0.00747 X	–0.372	–0.401	0.138
	ROS	7.69991 – 0.00601 X	–0.451	–0.505	0.203
Private JSC "Kyiv Confectionary Factory "Roshen"	*ROA*	1.21434 + 0.00023 X	0.087	0.152	0.008
	ROE	1.66710 + 0.00054 X	0.127	0.222	0.016
	ROS	14.56597 – 0.00265 X	–0.815	–2.436	0.664
PJSC "The house of vintage cognacs "Tauria"	*ROA*	11.04227 – 0.04066 X	–0.620	–1.369	0.385
	ROE	31.79628 – 0.11103 X	–0.606	–1.319	0.367
	ROS	30.16522 + 0.05660 X	0.303	0.551	0.092
PJSC Confectionery Factory "Kharkivyanka"	*ROA*	3.10429 + 0.01155 X	0.029	0.041	0.001
	ROE	9.57429 – 0.01425 X	–0.014	0.020	0.000
	ROS	3.38143 + 0.01528 X	0.037	0.052	0.001
PJSC "Kremenchug confectionery factory"	*ROA*	0.63524 – 0.00221 X	–0.547	–1.132	0.299
	ROE	1.61303 – 0.00518 X	–0.561	–1.174	0.315
	ROS	8.51365 + 0.00070 X	0.138	0.242	0.019
PJSC "Sumy food products factory"	*ROA*	–17.96081 + 0.30246 X	0.542	1.117	0.294
	ROE	–41.18742 + 0.68167 X	0.479	0.945	0.230
	ROS	5.98658 + 0.02400 X	0.104	0.181	0.011

* Author's calculations based on official data [21]. It is marked here r – coefficient of pair correlation between X and Y, t – t- Student's criterion, r^2 – coefficient of determination.

We propose to analyze the correlation-regression calculations at first according to the coefficient of determination r^2. Only three coefficients of determination correspond to the value of a regressive model of satisfactory quality: r^2=0.717 (*ROE*, PJSC "Karlsberg Ukraine"); r^2=0.838 (*ROS*, PJSC "Obolon"); r^2=0.664 (*ROS*, Private JSC "Kyiv Confectionary Factory "Roshen"). If the coefficient of determination r^2=0.838 for PJSC "Obolon", this means that the variation in the *ROS* for 83.8% due to the variation in the insurance costs, the share of not taken into account other factors remains 16.2%. That is, the cost of insurance determines the variance of the profitability of the listed enterprises, respectively for 71.7 %, 83.8 %, and 66.4 %, which has a rather significant effect.

The lower values (the interval r^2 for 0.1-0.5) of the determination coefficient are fixed in nine cases: within the limits of the minimum value r^2=0.103 for *ROS* to the PJSC "Pologovsky Oil Extraction Plant", and to the maximum r^2=0.496 for *ROE* to the PJSC "Kyivkhlib". The insurance costs determines the profitability and efficiency of such enterprises only by 10.3% and 49.6% respectively. In this case we can conclude that the proposed regression model is of low quality, and the share of insurance costs does not significantly affect the indicated performance indicators.

The least impact on insurance costs related for the others of the FIEs, where the determination coefficients $\mathbf{r^2}$ were less than 0.1.

The density of the relationship between the investigated parameters of the regression equation, which is determined by the Pearson correlation coefficient **r**, confirms the analysis results on the basis of the coefficient of determination $\mathbf{r^2}$. The analysis shows a direct proportional relationship between *ROE* and insurance costs for PJSC "Karlsberg Ukraine", and the inverse proportionality between ROS and insurance costs for PJSC "Obolon" and Private JSC "Kyiv Confectionary Factory "Roshen".

Analysis of the impact of insurance costs share on profitability

Let X share of insurance costs S_1 (table 4), and the target function of the analysis (dependent variable Y) – profitability indicators *ROA, ROE, ROS* (table 1). Let perform a hypothesis test for this case. Equation of pair linear regression was constructed in the form of dependence Y=A+BX. The corresponding calculations are given in Table 6.

Thus, the analysis confirms the second proposed hypothesis about the existence of a dependence between the competitiveness of the FIEs and the portion of money allocated to the insurance. This hypothesis can have confirmation for FIEs with high efficiency of doing business.

Table 6

Indicators of correlation-regression analysis of profitability (Y) and the share of insurance costs (X) for FIEs of Ukraine for 2013-2017*

Enterprise	Y	Regression equation Y = A + B X, %	r	t	r^2
PJSC "Karlsberg Ukraine"	*ROA*	28.14066 – 28.14617 X	–0.577	–1.224	0.333
	ROE	35.04222 – 22.62293 X	–0.147	–0.257	0.022
	ROS	19.60638 + 71.60377 X	0.729	1.846	0.532
PJSC "Obolon"	*ROA*	–9.93574 + 47.79888 X	0.073	0.127	0.005
	ROE	–68.84353 + 231.05093 X	0.049	0.085	0.002
	ROS	12.38136 + 231.96806 X	0.924	4.182	0.854
PJSC "Kyivkhlib"	*ROA*	9.00738 – 491.94399 X	–0.761	–2.035	0.580
	ROE	31.85167 – 1687.78418 X	–0.824	–2.523	0.680
	ROS	23.94915 + 40.15651 X	0.218	0.386	0.047
PJSC "Pologovsky Oil Extraction Plant"	*ROA*	0.87103 + 1.94349 X	0.266	0.478	0.071
	ROE	4.50302 + 4.79535 X	0.216	0.383	0.047
	ROS	17.50932 – 1.99752 X	–0.264	–0.475	0.070
Private JSC "APK–INVEST"	*ROA*	46.45545 – 313.86218 X	–0.711	–1.751	0.505
	ROE	94.41423 – 616.05769 X	–0.520	1.055	0.271
	ROS	87.46645 – 585.70221 X	–0.708	–1.734	0.501
PJSC "Zhytomyr Butter Factory"	*ROA*	19.63317 – 144.15929 X	–0.388	–0.730	0.151
	ROE	23.85982 – 150.88496 X	–0.368	–0.686	0.135
	ROS	22.93319 + 45.92920 X	0.371	0.692	0.138
PJSC "Kharkiv Biscuit Factory"	*ROA*	20.82708 – 370.06494 X	–0.349	–0.645	0.122
	ROE	22.99409 – 415.90909 X	–0.368	–0.685	0.135
	ROS	13.10688 + 122.59740 X	0.416	0.793	0.173
PJSC "Dniprovsky starch flour combine"	*ROA*	9.35890 – 48.35527 X	–0.890	–1.951	0.792
	ROE	17.49195 – 83.37520 X	–0.691	–0.955	0.477
	ROS	11.99398 – 60.13525 X	–0.750	–1.135	0.563
Private JSC "Kyiv Confectionary Factory "Roshen"	*ROA*	–2.08845 + 9.86740 X	0.601	1.304	0.362
	ROE	–3.81466 + 16.83396 X	0.636	1.429	0.405
	ROS	14.96441 – 8.74069 X	–0.429	–0.822	0.184
PJSC "The house of vintage cognacs "Tauria"	*ROA*	4.97292 – 11.53429 X	–0.320	–0.584	0.102
	ROE	15.87963 – 35.90908 X	–0.356	–0.660	0.127
	ROS	29.30725 + 78.43663 X	0.763	2.043	0.582
PJSC "Confectionery Factory "Kharkivyanka"	*ROA*	10.64353 – 188.35043 X	–0.656	–1.228	0.430
	ROE	27.12598 – 518.76875 X	–0.721	–1.471	0.520
	ROS	11.70500 – 203.00710 X	–0.682	–1.318	0.465
PJSC "Kremenchug confectionery factory"	*ROA*	0.77378 – 3.50596 X	–0.704	–1.717	0.496
	ROE	1.85433 – 8.01426 X	–0.705	–1.720	0.497
	ROS	9.07599 – 0.34630 X	–0.056	–0.096	0.003
PJSC "Sumy food products factory"	*ROA*	–4.95702 + 14.54509 X	0.645	1.463	0.416
	ROE	–12.13850 + 34.10277 X	0.594	1.278	0.352
	ROS	6.84205 + 2.05496 X	0.220	0.390	0.048

*Author's calculations based on official data [21]. It is marked here r – coefficient of pair correlation between X and Y, t – t- Student's criterion, r^2 – coefficient of determination.

Conclusions

The paper has analyzed the dynamics and structure of insurance costs and tests hypotheses concerning the impact of insurance on the efficiency of the activity of the insurance company, and also the role of insurance was explored to improve the security of the food market. The study describes the indicators of the efficiency and competitiveness of FIEs of Ukraine during 2013-2017.

The analysis confirms the hypothesis that FIEs with higher competitiveness are more prone to insurance. The hypothesis about the existence of a dependence between the competitiveness of FIEs and the portion of money allocated by FIEs for insurance is confirmed only for FIEs with high efficiency of doing business.

The results of the study are summarized by the following conclusions:

1. The analysis showed that the investigated FIEs do not violate the norms of the current antimonopoly legislation of Ukraine.
2. Among the selected list of food industry enterprises, the largest market share and share in the food industry as well as in Ukraine's GDP has PJSC “Karlsberg Ukraine”. The share of the company in the market is 1.173% of the food industry and 0.220% of Ukraine's GDP.
3. High performance and profitability indicators were related to the PJSC “Karlsberg Ukraine”. At the same time for PJSC “Obolon”, PJSC “Kyivkhlib”, PJSC “Sumy food products factory”, PJSC “Pologovsky Oil Extraction Plant” and for PJSC “Kremenchug confectionery factory” these indicators for some periods could be regarded as indicators of loss.
4. The low value of the profitability of the food industry enterprises of Ukraine can be explained both by internal factors and external problems.
5. Insurance costs insignificantly change the total production costs and, consequently, moderately affect the formation of the profit of the FIEs: the largest share of insurance costs 2.173% was for PJSC “Pologovsky Oil Extraction Plant” in 2016.
6. The rates of change of the insurance costs for FIEs during 2013-2017 were in range from -99.6 % (PJSC “The house of vintage cognacs “Tauria”), and to 881.4 % (PJSC “Pologovsky Oil Extraction Plant”) in 2014-2015.
7. The analysis does not fully confirm the hypothesis that “the main players in the food industry with a higher competitiveness are more prone to insurance”.
8. The hypothesis of the existence of a relationship between the competitiveness of the FIEs and the part of the money allocated to the insurance business can only be confirmed for FIEs with high-efficiency business case.
9. Result of the study the use of insurance as a tool to increase food market security confirms its high efficiency.

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Relation of qualitative and quantitive levels of availability and adequacy of food in determing the level of food safety

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Abstract

Introduction. It is necessary to have a set of indicators that will allow to consider qualitive and quantitive approaches for food availability and adequacy assessment for qualitative analysis of food safety.

Materials and methods. The object of the research is the analysis of food safety and indicators of food adequacy and availability by which it is carried out. Methods of statistical analysis in the part of designing trends of the share of food consumption in total households expenditures for 2000–2017 with the defining it sanalytical equation and the cost per unit of energy of the daily diet consumer prices in Ukraine were used during the research.

Results and discussions. The physical aspect of availability to food is determined by the possibility of the country to produce and deliver the food products of corresponding quality to the population and in the volume, which is necessery for providing of valuable person's nutrition. Economic aspect is determined by purchasing power of the population, id est by possibility to buy at the market or produce personally foodstuffs in the appropriate quantity and assortment, that provide the normal standard of person's living. For estimation of physical availability, the norms of overhead between rational or optimal nutrition, norms of minimum food consumption, calorie content of food of person's ration, providing of calorie content % of dayly ration due to the consumption of animal origin products are used. For estimation of economic availability standard of prices on foodstuffs, specific proportion of charges on foodstuffs in the combined charges of households, coefficients of nutrition differentiation according to social groups are used. They do not represent the state of food availability in complete measure. Thus, the calculations showed that in Ukraine, in 2000, 1% of total food exenses in the budget of totaled household expenses accounted about 41 kcal, then in 2017–52.5, which is 28% of the 2000 level. So, the availability of food in 2017 improved compared with 2000. The growth rates of 1,000 kcal, which in 2000–2014 and 2017 the growth rates of consumer prices increased, which is evidence in those periods not the price generates food availability as the level of income, especially in terms of food costs.

Conclusions. The complex use of these indexes will allow more fully estimate the level of food availability of population and work out the events of timely prevention of the educed threats.

Introduction

Food safety envisages, that the government must guarantee the production of sufficient amount of food for satisfaction of population's growing necessities. Thus, without obstacles and at the reasonable prices foreign trade must satisfy population's necessity with specific products that is not produced into the country, due to import. The functioning of the certain system of providing necessary backlogs with the aim of implementation of unexpected downstreams or sharp rises in prices is also envisaged. An important value is acquired by the physiology and solvent limits of demand on foodstuffs at the internal market that is characterized by the indexes of existent pattern of consumption and its physiology norms. Social aspect embraces the question of solvent access of population to food nutrition, social defence of scanty categories of population, strengthening of social politics addressness, achievement of equal level with city's terms of getting the real money incomes and social service, equal terms of public welfare in the village for all groups of population regardless of labour type activity and residence and other.

Undertaken research is based on the materials of the last publications, that concern the different aspects of determination and forming of food safety in the different countries of the world. Theoretical basis of the article is based on the defined notions of essence, structure, public policy and program of forming and development of food safety, that was considered in such researches: [1–4].

World experience of food safety forming was integrated in the documents of Food and Agriculture Organisation: [5–7].

The questions of research of food safety development status in Ukraine that define its basic problems, ways of their approaches to the government control of this area are studied by the following researchers: [8–11].

Important for undertaken the research was determination of methodical approaches for the evaluation of food availability level of population. In numeral researches of scientists, the questions of systematization of indicators for the evaluation of food safety overall, in particular it was carried out and were examined in the next researches: [12–16].

Analysis of these publications allowed to make conclusion, that the system of evaluation of food availability needs further development and expansion from position of combination of two aspects of physical and economic availability.

Materials and methods

The object of reseach is the analysis of food safety and indicators by which it is carried out. Indicators of food availability and adequacy are considered in details among the indicators adopted for food safety assessment.

Methods. For estimation of physical accessibility, the norms of the upper limit or optimal nutrition, norms of minimal food consumption, caloric content of human food rations, % of caloric intake of the daily ration of animal origin are sued. To assess the economic availability: the level of food prices, the share of food costs in total household expenses, the rates of nutrition differentiation by social groups. The analysis of existing approaches has allowed to offer additional for more complete qualitative and quantative analysis of adequacy and availability of food. The calculation of the proposed indicators was carried out on the example of Ukraine. The results of the research can be applied to other countries.

During the research, the methods of statistical analysis of existing indicators of food availability and sufficiency on the example of Ukraine were used.

The statistical analysis was used for developing of trends of the share of food expenditure in total household expenses for 2000-2017, with its analytical equation, the trend of the unit of energy of the daily diet and consumer prices on the example of Ukraine. The purchasing power of 1 kcal was calculated by the formula:

$$K = \frac{Kcal}{SV}$$

where K is the quantity of kcal, which accounts for 1% of the cost of food for the population in the total household expenses; Kcal – number of kcal energy of the daily diet of the average consumer; SV is the share of food expenditure in the total amount of total household expenses. The average cost of 1,000 kcal consumed (Vkcal) was calculated by the formula:

$$Vkcal = \frac{FV}{Kcal}$$

where FV – daily food expenditure in the total household expenditure per person.

Comparative analysis is used for correlation of trends of average cost of 1 thousand kcal and consumer price index for food.

Results and discussions

Principles of food safety forming and food availability as its part

Food safety is the level of food providing of population, that guarantees socio-political stability in society, survival and development of nation, person, families, steady economic development of the country. Food security is defined as the state in which people at all times have physical, social and economic access to sufficient and nutritious food that meets their dietary needs for a healthy and active life [17].

It expresses security of vital interests of a person that is expressed in guaranteeing of unimpeded economic access of a person by the state to the foodstuffs with the aim of maintenance of its ordinary vital activity.

In accordance with the draft law of Ukraine «About food safety of Ukraine» such basic principles of food safety forming are determined [18]:

1. Providing of interests of Ukraine in the system of international food safety in the conditions of globalization and regional economic integration;
2. Food independence of the country;
3. Economic validity of the national necessities which is related with providing of Ukraine with food, sufficientness and stability of food supplies;
4. Timelinesses and adequacy of events in relation to forming of food safety to the real and potential, internal and external threats;
5. Physical and economic availability of quality and safe food products for all categories of population in the amount of necessary for providing of active and healthy life.

These principles can be grouped according to the functional loading in relation to implementation of certain tasks in forming of food safety. Namely, thus: self-sufficiency; physical sufficientness; economic availability; balanced; quality; ecofriendlyness.

Thus, food safety is regarded as a science, policy, environmental and social program [19].

Self-dependance. Every country must provide population being based on the own production of basic foodstuffs. Food self-dependance envisages satisfaction of basic part of requirements in foodstuffs, that predetermines independence of the country from external suppliers in satisfaction of population necessities due to domestic production. This principle envisages the absence of dependence on the import of food stuffs. For prevention of dependence situation the country can grow the economic potential and promote efficiency of agroindustrial production. To achieve this, it is needed larger harvest of crops, vegetables and livestock products, with predictable increase of meat consumption per capita (kg/ person/ year) of 37 kg nowadays up to about 52 kg in 2050 (26-44 kg) in developing countries [20].

The main feature that at the same time there must be presented and imported commodities at the domestic market, in fact the consumer has a right for choice, and domestic commodity will become competitive only in the case, when will be distinguished by quality and contemporaneity of assortment. The substantiation of the UK food safety program provided the identification of priority research issues with a focus on food industry development [21].

The physical sufficientness means possibility of population to buy at the market or produce in the personal household foodstuffs that are needed in the appropriate quantity and assortment, that needed for satisfaction of human physiology necessities. Under vital necessary of foodstuffs we understand such products without which population can not exist, in particular, that: compensate the charges of organism energy in the process of its vital functions; assist natural recreation and active longevity of population; give an opportunity to provide harmonious development of children physiologically; assist prophylaxis and treatment of different diseases. The physical sufficientness of food envisages its trouble-free entering places of consumption in volumes that answer solvent demand and physiology norms. According to the Global Food Security Index (GFSI) methodology, availability is shown as such that easures the sufficiency of the national food supply, the risk of supply disruption, national capacity to disseminate food and research efforts to expand agricultural output [17].

Economic availability means access to the food resources of all layers of population due to present solvent demand. According to the Global Food Security Index (GFSI) methodology, affordability is shown as such that measures the ability of consumers to purchase food, their vulnerability to price shocks and the presence of programmes and policies to support customers when shocks occur [17].

The determinative factor of economic availability of food is the level of economic and social development of country's society. Possibility of different layers of population to consume foodstuffs in necessary volume and assortment depends on it, purchasing them on market prices, producing in own subsidiary households and others like that. There is the permanent deepening of differentiation of population income in Ukraine, so as the difference between extreme groups with the lowest and the greatest levels of income is substantial enough. The increase of economic availability of food nutrition must be founded, first of all, on the increase of population income, foremost its poorest layers and the reasonable suggested retail prices on foodstuffs, and also to the powerful program of their budgetary address support [22]. However, the relationship between food prices and income of the population is not always predictable, that is, the convenience and availability of food in particular place also play an important role [23].

Quality envisages providing of such totality of products properties that is stipulated to satisfy its ability to satisfy the necessities in accordance with setting appropriation. Realized through the achievement of valuable level of food nutrition of population due to the

consumption of high-quality foodstuffs. Quality, as an economic category is one of the basic factors of products competitiveness of agrarian sphere, and the problem of its increase is complex, so as it includes scientific, technical, social and economic parts [24]. Presently, it is impossible to produce quality goods without the use of high-quality agricultural raw material, innovative technologies and modern equipment and highly skilled personnel.

Balanced. The balanced food is based on that the meal consists of different food substances: fats, proteins, carbohydrates, vitamins, fat acids, mineral salts, microelements and others like that [25]. Irreplaceable substances, that does not appear in the person's organism, but get there with foodstuffs, have the special value. Irreplaceable amino acids and fat acids (linolic, linolenic) belong to such substances. To the group of irreplaceable substances vitamins, mineral elements that support and balanced molecular composition of different fabrics of person's organism, take also, compensating their losses in the process of vital functions. On the basis of the balanced food theory the daily allowance norms of the use of separate substances are worked out [26]. The principle of balanced also includes calorie content of foodstuffs. Calorie content shows the power value of food products or rations of food: the amount is warm, that it is distinguished by food or forage substances, when they oxidize in the organism of a person or animal. Safety of food and calorie content are basis of providing normally food nutrition of population.

Ecofriendlyness. We consider that it is important to add another constituent in the system of the country's food safety principles. According to the principle of ecofriendlyness all must be submitted to the principle of minimum loading on ecology and maximal "naturalness" of both product and process of foodstuffs production. Also the ecofriendlyness envisages that the consumption of electro- and heat power is taken to the minimum due to the events on energy-savings and use of energykeeping technologies. Now it is a niche of small farms and middle sizes plants. But a niche broadens constantly, as consumers are ready to overpay for a natural product without chemistry and for the idea of nature maintenance. Although, nowdays in Ukraine this is mainly fascination for solvent people and fashion statement, but annually production of ecological goods cost decrease and they become accessible to greater amount of consumers. Environmental agriculture is closely connected with nutrition and health and health must be seen as economic resource [27].

On the basis of the considered principles the group of indicators that characterize the certain degree of country's food safety providing is formed.

Essence, aspects and threats of food availability

Availability as category means reaching desirable for a person. Food availability needs to be examined in physical and economic aspects. Physical aspect is determined by possibility of the country to produce and deliver food products to population in the volume, to the necessity of valuable food nutrition providing for a person, corresponding quality. Economic aspect is determined by purchasing power of population, id est by possibility to buy at the market or produce in the personal household foodstuffs in appropriate quantity and assortment, that provide the normal standard of living and person's health. It is access to the food resources of all layers of population due to present solvent demand.

The main factors of threat to food safety are existence of groups of population, that are under the limit of poverty and do not have sufficient income for purchasing of minimum set of foodstuffs; the structural unbalanced food nutrition according to separate constituents; low and unstable quality of foodstuffs; exhaustion of domestic agrarian production potential simultaneously with its technological degradation. Therefore, the increase of economic and physical food availability on the basis of increase of foodstuffs production and improvement

of their quality volumes is strategic priority of social and economic development of the country.

Physical availability

Index of physical availability is the relation of physical and desirable levels of food consumption. Desires of everybody in this sphere can be inefficient or indefinite. For this purpose there are the so-called the special purpose of reference-points, namely medical norms of food nutrition. Such norms are developed by specialists on the hygiene of food nutrition for aged and professional groups, geographical and social terms are taken into account.

There are two kinds of nutrition norms [28]:

1. Norm of top level between rational or optimal food nutrition, exceeding of that generates the problems of overnutrition and overweight. The achievement of such norms means that the task of food availability is attained and takes place the state of population's food providing.
2. Norms of minimum food consumption, that determine the lower limit of necessary receipt of nutritives. Such norms are examined as a cut-off norms.

The norms of top limit of rational food nutrition have character of recommendations. The minimum norms of food consumption accounts in Ukraine on the basis of law "About Cost of Living" and become firmly established by the resolution of Cabinet of Ministers [28].

The level of the population's consumption of food products is determined as the combined index of actual consumption of separate types of food products in calculation per capita, and also dayly calorie content of food ration, taking into account its balanced on maintenance proteins, fats, carbohydrates, vitamins, macro- and microelements [29].

The level of physical availability can be estimated by means of estimation of satisfaction level of foodstuffs consumption to the rational norms (Table 1).

Table 1

State of physical availability of food

Food Products	Average food consumption per capita per month, kg				Indicator of consumption adequacy,%			
	2000	2010	2015	2017	2000	2010	2015	2017
Meat and meat products	3,3	5,1	4,6	4,7	49,3	76,1	68,7	70,1
Milk and milk products	17,1	19,2	19,8	19,3	53,9	60,6	62,5	60,9
Eggs	18	20	19	20	74,4	82,6	78,5	82,6
Fish and fish products	1,3	1,7	1,2	1,3	76,5	100,0	70,6	76,5
Sugar	3,5	3,1	2,8	2,8	109,4	96,9	87,5	87,5
Oil and other vegetable fats	1,8	1,8	1,6	1,5	163,6	163,6	145,5	136,4
Potatoes	10,4	7,6	6,6	6,4	101,0	73,8	64,1	62,1
Vegetables and melons	9,5	10,3	8,8	8,5	70,9	76,9	65,7	63,4
Fruits, berries, nuts, grapes	2,5	3,5	3,1	3,7	33,3	46,7	41,3	49,3
Bread and bread products	10,7	9,3	8,5	8,4	127,4	110,7	101,2	100,0

Data for 2015, 2017, excluding part of the temporarily occupied territories in the Donetsk and Luhansk oblasts

Source for calculation: [30]

An analysis showed that the most critical level of physical availability in Ukraine was observed for fruit, berries, nuts and vine. On meat and meat products, milk and milk products, potato, also there is a level of the dissatisfied consumption of vegetables. The reasons of such situation is low investment attractiveness of market through the necessity of considerable capital, high risks and absence of country's support of agricultural producers at presence of low purchasing power of population. The consumption of eggs, sugar is close to rational norms, on bread is the same. According to oil and other vegetable oil, we exceed the norms of rational consumption considerably.

On the estimations of FAO and Worldwide Organization of Health Protection, the middle norm of food nutrition for one person must present 2300-2400 kcal on the period of twenty-four hours [5]. This index differs depending on sex, age, profession, and also natural and climatic conditions. In the case, when the index becomes below than 1800 kcal, then the clearly expressed malnutrition is shown up, and when this index passes the limit to 1000 kcal on the period of twenty-four hours is obvious hunger (physical shortage of meal) [31]. Reasons of hunger are natural, political cataclysms, wars, financial crisis, reduction of consumption through uneven distribution of food.

From data of FAO food nutrition must be valuable and in the structure of food ration the norm of albumen content must be not less of 100 gs on the period of twenty-four hours [31]. Food nutrition, when we have the lack of not only calories but also proteins, first of animal origin, and also fats, vitamins, microelements, is called poor nutrition. It is conditioned by permanent malnutrition and monotony of ration (one type of product prevails in the consumption).

It is necessary to notice that in the USA this index presents 3900 kcal, in the countries of European Union is 3500 kcal [32]. The actual middle index of calorie content of food ration in the world presents 2700 kcal on the period of twenty-four hours, in the economically developed countries is on the average about 100 grams present per capita is 3400 kcal, and consumption of proteins on the period of twenty-four hours. It is important to mark, that in the developed countries there are social groups with a proof low level consumption that need permanent help from the side of the country [33]. For the analysis of the diet balance, we use the average daily caloric intake of the ration of the entire population with the definition of its parts at the expense of products of animal and plant origin, without taking into account gender, age, occupation and climatic conditions. Such simplification does not limit the quality of the conclusions, since in the future there is the comparison of the average daily caloric value from the calculation for the whole population and the average household expenditure on food as well on average per person.

The maximum (cut-off criterion) criterion of daily calorie content of food ration in Ukraine presents 2500 kcal on period of twenty-four hours [29], thus 55 % of daily ration must be provided due to the consumption of animal origin products (table 2).

As it is shown from the table 2 all investigated years the calorie content of population ration of Ukraine was higher than maximum level of 2500 kcal. After the economic crisis of 2008-2009 the calorie content of foodstuffs consumption decrease gradually, military situation in Ukraine after 2014 also complicated proceeding in calorie content of ration of average Ukrainian person.

On the whole, in 2017 the population of Ukraine consumed foodstuffs calorie content which is on 8,3 % more than maximum level. However, other situation with the pattern of consumption, as 55% must belong to the products of animal origin. In Ukraine this norm is not executed, for investigated period Ukrainians consumed at most 41% in 1990 and minimum 23% in 2000 of foodstuffs of animal origin. The positive tendency is that at the beginning of 2000 of foodstuffs of animal origin consumption increases gradually. In 2017 due to the products of animal origin the average daily food value of ration presented 28,9 % instead of recommended 55% of general ration.

Table 2

Dynamics of caloricity of average daily consumption of food products by the population of Ukraine per capita, kcal

Indexes	2000	2005	2010	2015	2016	2017
Total caloric content	2661	2916	2933	2799	2742	2707
% to the limit level (threshold level 2500)	106,4	116,6	117,3	112,0	109,7	108,3
Caloric content of products of animal origin	611	733	809	791,0	790,0	781,0
% to total caloric content	23	25,1	27,6	28,3	28,8	28,9
% to the limit level (boundary level 1365)	44,8	53,7	59,3	57,9	57,9	57,2
Caloric content of vegetable products	2050	2183	2124	2008	1952	1926
% to total caloric content	77	74,9	72,4	71,7	71,2	71,1

Data for 2015, 2017, excluding part of the temporarily occupied territories in the Donetsk and Luhansk oblasts

Source for calculation: [34]

Economic availability

Considerable part of food in rural locality and its greater part in cities are bought, then price in the prominent factor of economic food availability. Satisfaction of consumers' necessities and successful realization of commodity suggestion depend on the cost of product, that can be examined in two aspects: from the point of view of consumers and from the point of view of businessmen that produce and will realize the prepared or finished products. For consumers the price means possibility in different measures to satisfy their necessities. Consumer is ready to pay higher price for the products of high quality. From the point of view of businessman, acceptable price gives the opportunity to realize finished products and get sufficient profit.

One of food safety indicators of the country is determining the specific ratio of charges on foodstuffs in the combined charges of households, it must not exceed 60% (Figure 1). The critical limit of gross income use of economies is determined at this value.

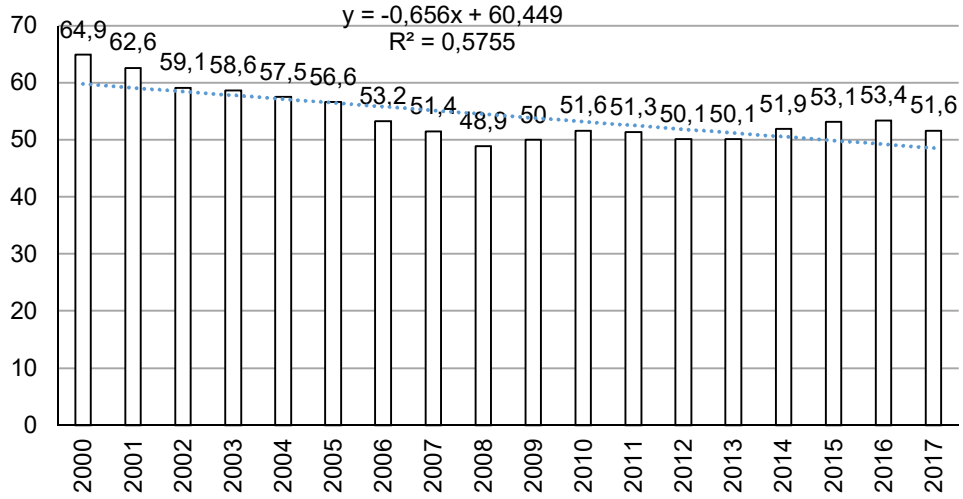

Figure 1. Specific weight of food expenses in total household expenses for 2000-2017 years
Data for 2015, 2017, excluding part of the temporarily occupiedterritories in the Donetsk and Luhansk oblasts
Source for calculation: [30]

In 2000-2001 critical value of this index was observed, after this there was a descending tendency to 2008, after that an insignificant increase took place in 2017 - this index is presented 51,6%. Worsening of price food availability compelled the population to promote part of food charges in family budget. In world statistics such part serves as the important indicator of the level of country's development. For the poorly developed countries the low level of consumption of food combines with high part of food products charges in the lump sum of family's charges. Thus, in 2017 it presented 13,4% in France, 8,1% in Great Britain, 17,1 % in Poland, 22,2% in Lithuania. The average value of this index in the countries of EU- 28 in 2017 was 12,2% [35].

Important aspect of food safety is availability of valuable nutrition for population with low-income. There is certain differentiation in the consumption of foodstuffs by the population of Ukraine, that it is also possible to define by means of special indicator which is determined by the resolution № 1379 [29].

The index of differentiation of nutrition cost according to social groups is accounted as a correlation between by the nutrition cost of 20% of households with the largest income and cost of nutrition of 20% of households with the least income (Table 3).

The main differentiation of foodstuffs consumption is observed in the groups of fruit, berries, nuts, grapes. Households of the fifth quintile group consume fruit and berries on the average more than in two times than households of the first quintile group. Also, wide difference in the consumption of meat and meat products (in 2017 more than 71%), milk and dairy products (more than 63%), fish and fish products (more than 50%), vegetables and melon-field (more than 52%). At the low middle level of food consumption its large differentiation destroys quality of food of the poorest layers of population for the cut-off criteria of food safety and it creates an impending condition. If to examine the tendencies of consumption differentiation, then in 2017 the decline took place only for meat, dairy products, eggs and fruit, for other products it became sharp.

Table 3

Differentiation factor of food by social groups

Food Products	2013	2014	2015	2016	2017
Meat and meat products	1,82	1,81	1,76	1,67	1,71
Increase / decrease to the previous year	-	*-0,01*	*0,05*	*0,09*	*-0,04*
Milk and milk products	1,67	1,62	1,62	1,70	1,63
Increase / decrease to the previous year	-	*-0,05*	*0,00*	*0,08*	*-0,07*
Eggs	1,28	1,22	1,24	1,29	1,22
Increase / decrease to the previous year	-	*-0,06*	*0,02*	*0,05*	*-0,07*
Fish and fish products	1,57	1,75	1,60	1,60	1,50
Increase / decrease to the previous year	-	*0,18*	*-0,05*	*0,00*	*-0,10*
Sugar	1,27	1,40	1,39	1,39	1,29
Increase / decrease to the previous year	-	*0,13*	*-0,01*	*0,00*	*-0,10*
Oil and other vegetable fats	1,19	1,20	1,13	1,21	1,07
Increase / decrease to the previous year	-	*0,01*	*-0,07*	*0,8*	*-0,14*
Potatoes	1,06	1,16	1,11	1,18	1,05
Increase / decrease to the previous year	-	*0,10*	*-0,05*	*0,07*	*-0,13*
Vegetables and melons	1,46	1,55	1,59	1,52	1,52
Increase / decrease to the previous year	-	*0,09*	*0,04*	*-0,07*	*0,00*
Fruits, berries, nuts, grapes	2,57	2,59	2,29	2,29	2,15
Increase / decrease to the previous year	-	*0,02*	*-0,30*	*0,00*	*-0,14*
Bread and bread products	1,09	1,12	1,05	1,08	1,02
Increase / decrease to the previous year	-	*0,03*	*-0,07*	*0,03*	*-0,06*

Data for 2015, 2017, excluding part of the temporarily occupied territories in the Donetsk and Luhansk oblasts

Source for calculation: [36]

Indicators of food availability providing

Important task of food safety is increase of quantitative and quality descriptions of population's food nutrition at simultaneous decline of specific proportion of charges on food in family budget. Quality description of sufficientness of food nutrition is average daily calorie content of ration of middle Ukrainian person, the index of physical sufficientness of food nutrition and purchasing power that is expressed as income can come forward as quantitative descriptions.

Thus, the integral index of nutrition availability can be the index of purchasing power of 1 kcal. It can be determined as a relation of amount kcal energy of daily food ration of average person's nutrition to specific ratio of charges on nutrition in the general volume of the combined charges of households. This index will be shown by what amount of kkal will be on 1% charges on food (Figure 2).

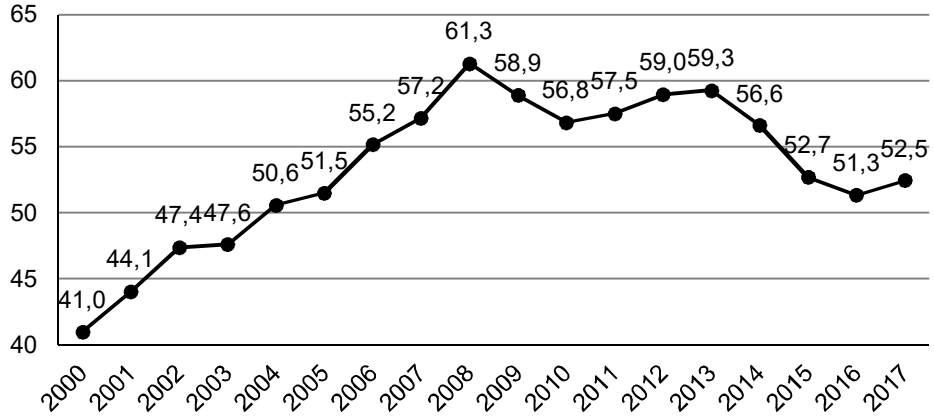

Figure 2. The amount of kcal that accounts for 1% of the total food expenditure of the population in the total household expenditure in Ukraine

Data for 2015, 2017, excluding part of the temporarily occupied territories in the Donetsk and Luhansk oblasts

Source for calculation [30]

From data of figure 2 it is possible to monitor as availability of nutrition changed during 2000–2017. Thus, if in 2000 on 1% of charges on food in the budget of the combined charges of households it was 41 kcal, then in 2017 – 52,5, that on 28% of the level of 2000. And availability of food nutrition in 2017 became better in comparison with 2000. It is interesting that according to this index it is possible to compare availability of food nutrition between separate regions and countries.

Thus, in the USA at daily consumption of food in 3800 kcal the specific proportion of charges on food in the income of households was 14,1% or 270 kcal on 1%. Accordingly on this index of food availability of the USA prevail Ukraine almost in 5 times [37].

Dynamics of energy unit cost of daily food ration of average person in comparison with cost-of-living-indexes also can serve as the important indicator of food availability that links the quality and quantitative level of nutrition availability (Figure 3). This index shows how the price and income are important for ordinary person's nutrition.

Thus, for 2010-2017 the cost of 1 thousands kcal had grown almost in 2,3 times, certainly inflation processes influenced on this in Ukraine. But, as the research showed, the rates of increase of 1 thousands kcal cost for investigated period except 2015-2016 passed ahead the rates of consumer price, it is certificate that not only price forms food availability but also the level of income forming. And the energy cost of daily ration grows quicker than inflation processes in the country.

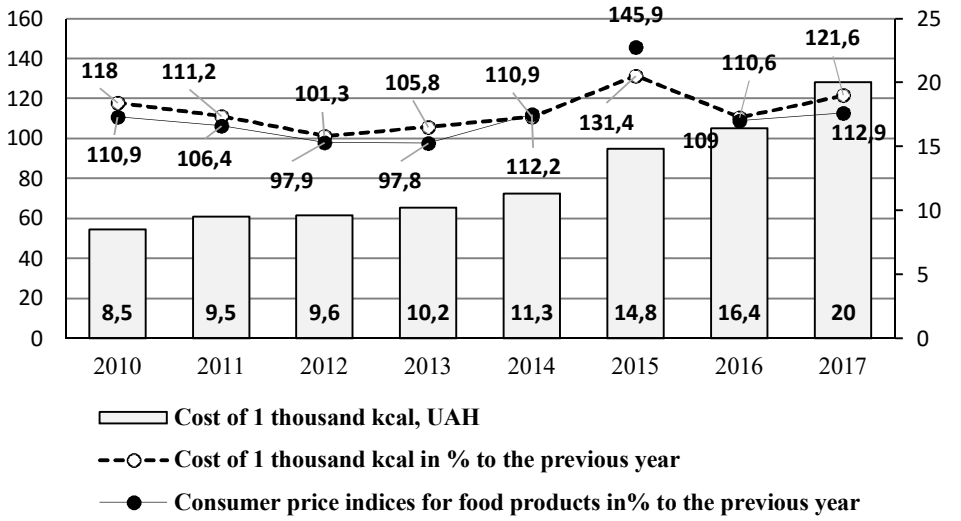

Figure. 3. Dynamics of cost per unit of energy of the daily diet and consumer prices in Ukraine
Data for 2015, 2017, excluding part of the temporarily occupied territories in the Donetsk and Luhansk oblasts
Source for calculation: [30; 36]

Conclusions

Reasons of unsatisfactory food availability of the country can be: deficit of food; low level of solvent demand, that is determined by the standard of prices and income; dependence of internal market on the imported food delivery; low level of products competitiveness in quality or/and by price at sufficientness of food of own production. It is important to monitor those tendencies correctly that in actual fact influence on this index.

Indicators of food availability, offered in this research, combine a physical and economic aspect and they differ from other existing.

The amount of kcal, that is on 1 % of expenses on population nutrition of households and the cost of energy unit on daily nutrition ration and its correlation in the combination of charges with the standard of consumer prices to other existent indicators of food availability will allow to monitor the problems that arise up in the country in relation to provide the population with food, and, accordingly, to develop events that are needed to use for availability of valuable and quality person's nutrition.

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Comprehensive analysis of food production efficiency using nanoparticles of nutritional supplements on the basis of oxides of two and three valence iron "Magnetofood"

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Abstract

Introduction. The complex analysis of the estimation of the efficiency of the new food product using the nanoparticles of the food additive "Magnetofood" on the basis of two and three valence iron oxides is presented.

Materials and methods. Food products made with the use of nanoparticles of two and three valence iron oxides "Magnetofod" (Fe_3O_4) were investigated using standard and commonly used methods of experimental studies (organoleptic indicators for a 5-point scale; moisture and fat removal capacity using a butyrometer and a refractometer; output the finished product for the difference of masses), expert analysis.

Results and discussion. The conducted researches indicate that the introduction of scientifically grounded food products with nanoparticles will allow to produce competitive products. The nutritional supplement "Magnetofood" has a significant functional and technological potential (sorption, antioxidant, bacteriostatic, emulsifying, stabilizing, foaming and gelling, water and fat-binding, water and fat-retaining properties), which causes the introduction of nanoparticles of supplements to recipes of bakery, flour confectionery, meat, pasty-marmalade products and cheesecakes and whipped desserts. It contributes to resource conservation during the production of food products, the formation of high consumer properties and increase the product yield and economic efficiency of its production. Food products made with the use of food nano additives "Magnetofood", has high organoleptic, functional and technological properties, extended shelf-life. According to the results of the comparative analysis of quality and price characteristics of food products with "Magnetofood" nanoparticles, it was concluded that new products has the more value for B2B consumers compared with analogues.

Conclusions. A high level of scientific, scientific, technical, social and economic efficiency of food products with the addition of a nutritional supplement "Magnetofood" based on oxides of two and three valence iron is proved.

Introduction

The experience of world leaders in the food industry [1] shows the urgency of introducing innovations into the practice of economic activity as one of the factors contributing to the competitiveness of the enterprise and its further development. The analysis of the trends in the food industry shows the active use of nanotechnologies in this area, the application of which in the production of food products is recognized as one of the most promising areas for the introduction of the results of nanosciences [2-6], in particular, changes in the qualitative and functional and technological characteristics of food products [7, 8]. According to [9], the global nanotechnology market will reach $ USA 125 billion by 2024. In the structure of demand for nanoproducts [3], the segments of the consumer market account for 5.0% of the food market. Researchers on nanotechnology commercialization point out that food industry enterprises are most prepared for the perception and implementation of nanotechnologies [2].

Innovative activity of food industry enterprises determines the relevance of research on methodological principles for evaluating the efficiency of innovative food technologies with nanoparticles. The results of this assessment contribute to the innovative activity of food industry enterprises and increase the validity of managerial decisions on the introduction of innovative products into production.

The analysis of literary data testifies to different positions of researchers regarding the criteria, indicators and methods of evaluation of innovation products in general and in the case of introduction of nanotechnologies in particular. Depending on the purpose of the evaluation, the criteria for the new product include the strategic feasibility, technical feasibility, consumer perceptions, market opportunities and financial performance [10], the uniqueness of the product, its market potential, and technical feasibility [11]; use indicators of safety [12], quality [13], prices of products [13, 14]. Conclusions regarding the effectiveness of the implementation of innovative developments are based on the principles of quality estimation, discounting of cash flows, expert assessments [13-16].

Since innovative food products using the Magnetofood nutritional supplement have a multidimensional nature, and their results are the subject of interest of a significant number of subjects (producers, consumers, investors, research institutions, etc.). To conclude on the feasibility of introducing these products into the practice it is advisable to use a set of criteria and indicators that reflect the interests of key players in the implementation of the innovation process.

The aim of the research is a comprehensive analysis of the effectiveness of innovative food products using a nutritional supplement "Magnetofood" based on two and three valence iron oxides by studying functional and technological properties, quality indices and output of finished products, scientific, scientific and technical efficiency and its implementation efficiency, value for the consumer.

To achieve this goal, the following tasks need to be addressed:

– to investigate functional and technological properties, product yield and organoleptic indices of food products using a rational quantity (0,15% by weight of raw materials) of a food additive "Magnetofood";
– to conduct a comprehensive analysis of the effectiveness of the introduction of innovative food products using a nutritional supplement "Magnetofood" based on two and three valence iron oxides.

Materials and methods

Materials

In the course of the research, food products with the addition of a nutritional supplement "Magnetofood" based on two and three valence iron oxides were used: bread and flour confectionery, minced meat product, sour-milk products, pasty and marmalade products, whipped fruit and desserts.

Methods

Food products using a nutritional supplement "Magnetofood" based on two and three valence iron oxides have been investigated using standard and commonly used methods of experimental studies, expert analysis.

The method of complex evaluation of the effectiveness of the introduction of food products with nanoparticles involves the following stages.

1. To form a group of experts.

To determine the effectiveness of the introduction of innovative food products with nanoparticles, form a group of experts, which include experts in the field of food technology. The number of experts (m) is determined by the formula:

$$m = \frac{t_a^2}{\varepsilon^2}, \quad (1)$$

where m – number of experts, persons;

t_α – the tabular value in accordance with the accepted confidence probability α;

α – confidence probability, %;

ε – maximum permissible error.

To determine the competence of experts, were used the methods of questionnaire survey and self-assessment.

2. To carry out an expert evaluation of innovative food products with nanoparticles on the criterion of scientific effectiveness.

To do this, were formed a questionnaire to include questions about the scientific level, novelty, depth of scientific developments and knowledge of products. Characteristics and scale for expert evaluation of the scientific effectiveness of innovative food technologies are given in Table 1.

Table 1

Characteristics and scale of evaluation of innovative food products with nanoparticles on the criterion of scientific efficiency

Indicator	Linguistic assessment		
	high level	average level	low level
	Scale for evaluation		
	3 points	2 points	1 point
Scientific level	A new direction of scientific knowledge and research has been created	Existing techniques have been improved	The existing theoretical positions are confirmed
Novelty	Fundamentally new results	Methods, ways to create new products	Solutions based on simple generalizations
The depth of scientific development	The hypotheses are theoretically substantiated and tested on a large amount of experimental data	Hypotheses are theoretically grounded and tested on a small amount of experimental data	Hypotheses are theoretically grounded
Knowledge of products	The coefficient of knowledge intensity exceeds the average value of enterprises of a certain type of economic activity	The coefficient of knowledge intensity corresponds to the average value of enterprises of a certain type of economic activity	The coefficient of knowledge intensity of products is smaller, the average value of enterprises of a certain type of economic activity

Developed on the basis of [12-14].

Calculate the coefficient of scientific efficiency (K_s) v:

$$Ks = \frac{\sum_{j=1}^{k}\sum_{i=1}^{n} B_{si}}{\sum_{j=1}^{k}\sum_{i=1}^{n} B_{si\max}}, \quad (2)$$

where K_s – coefficient of scientific efficiency;

B_{si} – actual value of the *i*-th indicator of scientific effectiveness, score;

$B_{si\max}$ – the maximum value of the *i*-th indicator of scientific effectiveness, the score;

n – the number of scientific performance indicators, units;

k – number of experts, persons. B_{si}

To assess innovative food products on the criterion of scientific efficiency to adhere to these conditions (Table 2).

Table 2

Estimation of innovative food products with nanoparticles on the criterion of scientific effectiveness

Value of the factor	Conclusion
$0 \leq K_s < 0{,}33$	Low level of scientific effectiveness of innovative food products with nanoparticles
$0{,}34 \leq K_s < 0{,}66$	The average level of scientific effectiveness of innovative food products with nanoparticles
$0{,}67 \leq K_s \leq 1{,}0$	High level of scientific effectiveness of innovative food products with nanoparticles

3. To carry out an expert evaluation of innovative food products with nanoparticles on the criteria of scientific and technical efficiency.

For this purpose, to formulate a questionnaire to include questions about the prospects of use, scale of implementation, period and degree of implementation of technologies of innovative food products with nanoparticles. Characteristics and scale for expert evaluation of scientific and technical efficiency of innovative food technologies are given in Table 3.

Table 3

Characteristics and scale of evaluation of innovative food products with nanoparticles on the criterion of scientific and technical efficiency

Indicator	Linguistic assessment		
	High level	High level	High level
	Scale for evaluation		
	3 points	2 points	1 point
Perspectives of use	Results can be found in many scientific fields	Results can be used to develop a particular scientific direction	Results can be used in applied research
Scale of implementation	National, world economy	Regional market	Local market, individual enterprises
Implementation period	Up to 3 years old	From 3 to 5 years	More than 5 years
Degree of implementation	The results are published in the form of scientific reports, formalized in the form of normative and technical documentation, introduced into practical activities	The results are formalized in the form of normative and technical documentation	The results are published in the form of scientific reports

Developed on the basis of [12-14].

Calculate the coefficient of scientific and technical efficiency (K_{st}) by the formula:

$$Kst = \frac{\sum_{j=1}^{k}\sum_{p=1}^{m} B_{stp}}{\sum_{j=1}^{k}\sum_{p=1}^{m} B_{stp\max}}, \quad (3)$$

where K_{st} – coefficient of scientific and technical efficiency;

B_{stp} – actual value of p-th indicator of scientific and technical efficiency, score;

$B_{stp\max}$ – maximum value of p-th indicator of scientific and technical efficiency, score;

m – number of indicators of scientific and technical efficiency, units;

k – number of experts, persons.

To assess innovative food products by the criterion of scientific and technical efficiency, to adhere to these conditions (Table 4).

Table 4

Estimation of innovative food products with the acquisition of criteria of scientific and technical efficiency

Value of the factor	Conclusion
$0 \le K_{st} < 0{,}33$	Low level of scientific effectiveness of innovative food products with nanoparticles
$0{,}34 \le K_{st} < 0{,}66$	The average level of scientific effectiveness of innovative food products with nanoparticles
$0{,}67 \le K_{st} \le 1{,}0$	High level of scientific effectiveness of innovative food products with nanoparticles

4. To carry out an experimental study of the quality of food products with nanoparticles of the additive "Magnetofood".

To do this, determine the organoleptic and functional-technological indicators by type of food products.

Calculate a comprehensive index of food quality by the formula:

$$Kqr = \frac{\sum_{j=1}^{k}\sum_{x=1}^{z} B_{xr}}{\sum_{j=1}^{k}\sum_{x=1}^{z} B_{xr\max}}, \quad (4)$$

where Kqr – coefficient of quality r-th products;

B_{xr} – actual value of the quality of r-th products in the x-th indicator, score;

$B_{xr\max}$ – the maximum value of the quality of r-th products in the x-th indicator, the score;

z – number of quality indicators, units;

k – number of experts, persons.

To identify the quality of innovative food products with nanoparticles, to adhere to these conditions (Table 5).

Table 5

Estimation of innovative food products with nanoparticles on the criterion of quality

Value of the factor	Conclusion
$0 < Kqr \leq 0{,}33$	The quality of innovative food products with nanoparticles is low
$0{,}34 < Kqr \leq 0{,}66$	The quality of innovative food products with nanoparticles is average
$0{,}67 < Kqr \leq 1{,}0$	The quality of innovative food products with nanoparticles is high

5. To carry out an expert evaluation of innovative food products with nanoparticles on the criterion of value for the consumer.

To do this, calculate the food value ratio by matching the quality and price availability factors.

The coefficient of price availability of innovative food products with nanoparticles is based on the formula:

$$Kpr = \frac{P_r}{P_{cr}}, \tag{5}$$

where Kpr – coefficient of price availability of *r*-th products;

P_r – the price of *r*-th products, monetary units;

P_{cr} – the price of a product-analogue of *r*-th products, monetary units.

The coefficient of value of innovative food products with nanoparticles for the consumer to calculate by the formula:

$$Kv = \frac{Kqr}{Kpr}. \tag{6}$$

To identify the value of innovative food products with nanoparticles for the consumer, to adhere to these conditions (Table 6).

Table 6

Estimation of innovative food products with nanoparticles on the criterion of value for the consumer

Value of the factor	Conclusion
$Kv > 1{,}0$	The high value of innovative food products with nanoparticles for the consumer; the benefits received by the consumer exceed the cost of purchasing the product
$Kv = 1{,}0$	Low value of innovative food products with nanoparticles for the consumer; the benefits received by the consumer correspond to the cost of purchasing the product
$Kv < 1{,}0$	The low value of innovative food products with nanoparticles for the consumer; the benefits that the consumer receives is less than the cost of purchasing the product

6. To carry out an expert evaluation of innovative food products with nanoparticles on the criterion of economic efficiency.

To do this, determine the growth of profitability of production per unit of output by the formula:

$$\Delta R_r = \left(\frac{P_{r1} - C_{r0}}{C_{r1}} \right) \times 100 - R_{r0}, \quad (7)$$

where ΔR – an increase in the profitability of *r*-food products in the event of the introduction of innovative technologies, %;

P_{r1} – the price of sales of *r*-innovation food products, monetary units;

C_{r0} – cost price of *r*-food products according to traditional technology, monetary units;

C_{r1} – the cost price of r-food products in the case of the introduction of innovative technologies, monetary units;

P_{r0} – the profitability of the r food in accordance with traditional technology, %.

7. Conclude on the effectiveness of the introduction of innovative food products with nanoparticles.

Results and discussion

In accordance with the methodology of the integrated analysis of the effectiveness of the introduction of innovative food products, as outlined above, the evaluation of innovative food products using the nanoparticles of a food additive "Magnetofood" based on two and three valence iron oxides was carried out, the results of which concluded that a high level of efficiency of the indicated innovation development.

The results of scientific work have significant potential not only in the food industry, but also in the field of production of cosmetic and pharmaceutical products, food products of medical and preventive action, indicating the prospects of using the scientific results obtained in many scientific fields and types of economic activity.

Innovative is not only the indicated theoretical and experimental scientific results, but also brought to the practical introduction into the economic activity of food industry enterprises new types of products that have a high level of knowledge intensity (Figure 1).

According to calculations, the coefficients of scientific and scientific and technical efficiency of food products made with the use of a nutritional supplement "Magnetofood" based on two and three valence iron oxides were 0.83 and 0.84 points, respectively, indicating a high level of scientific and scientific-technical efficiency developed innovative food products (Table 7).

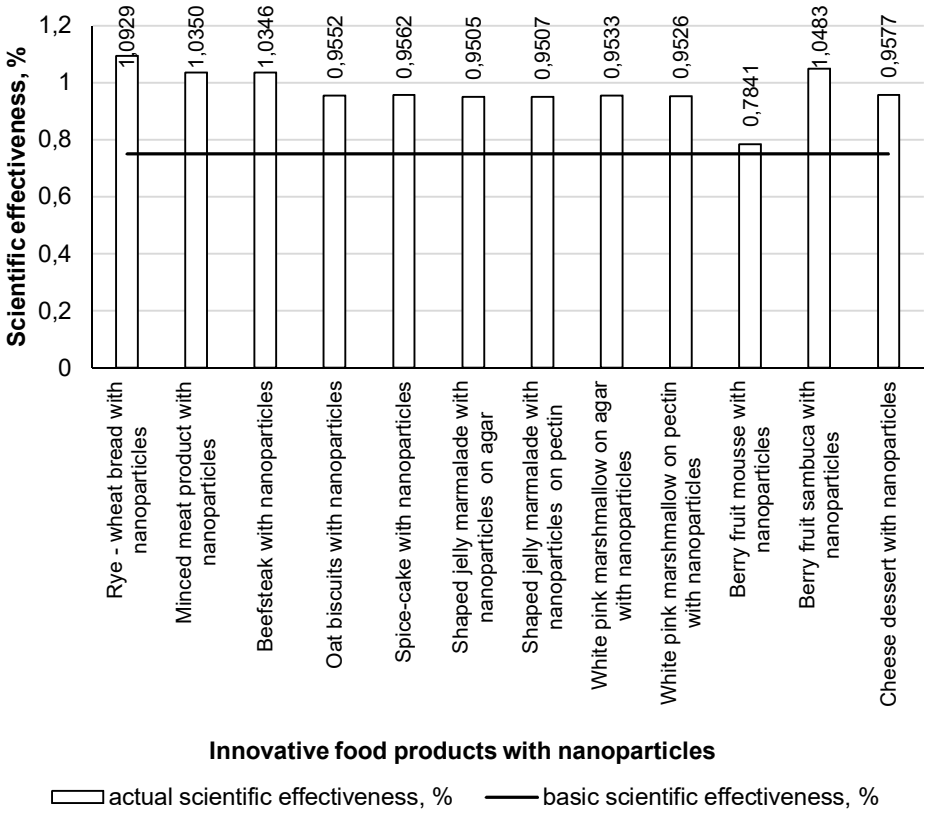

Figure 1. Indicators of scientific effectiveness of products based on the results of the introduction of innovative food products with the addition of 0.15% of a nutritional supplement "Magnetofood" based on two and three valence iron oxides, %

The most highly appreciated by experts were scientific efficiency and the prospect of using the results. The maximum values in these areas reached 0.88 and 0.90 points, respectively.

Based on the innovative idea of food products using nanoparticles, innovative products characterized by high organoleptic characteristics (Figures 2-13) and new functional and technological properties – sorption, emulsifying, structuring, foaming and gelling, stabilizing, water and fat-binding, water and fat-retaining properties (Table 8 and Figures 2–13). Experimental way is the rational mass fraction of nutritional supplement "Magnetofood" on the basis of two and three valence iron oxides in the formulation of food products, which is 0.15% of the mass of raw materials [19, 20].

Table 7

Results of expert evaluation of innovative food products using a dietary supplement "Magnetofood" based on two and three valence iron oxides on the criteria of scientific and scientific – technical efficiency

Indicator	Value, score		Coefficient
	maximum	actual	
Scientific performance			
Scientific level	3,0	2,4	0,81
Novelty	3,0	2,4	0,79
The depth and extent of the dissemination of ideas	3,0	2,5	0,83
Scientific efficiency of products	3,0	2,6	0,88
Together	12,0	9,9	0,83
On the average	3,0	2,5	0,83
Scientific and technical performance			
Perspectives of use	3,0	2,7	0,90
Scale of implementation	3,0	2,5	0,83
Implementation period	3,0	2,4	0,81
Degree of implementation	3,0	2,5	0,83
Together	12,0	10,1	0,84
On the average	3,0	2,5	0,84

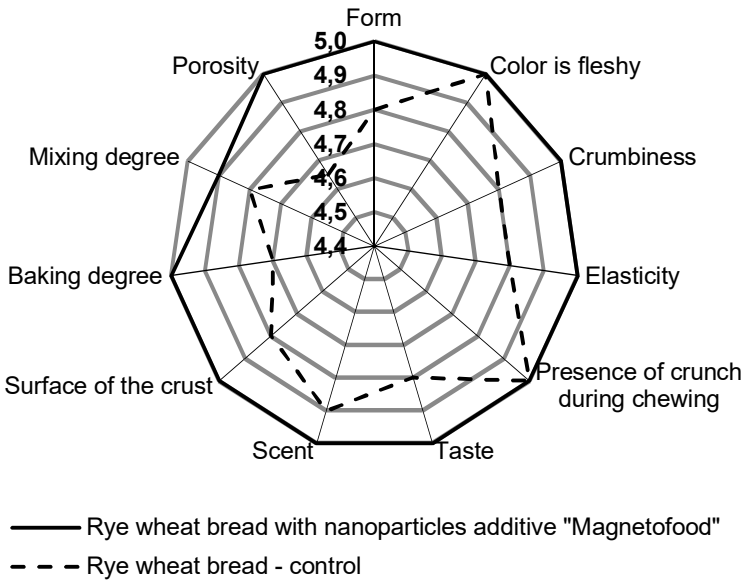

Figure 2. Levels of quality of organoleptic properties of rye-wheat bread with nanoparticles added to "Magnetofood" in comparison with control rye-wheat bread

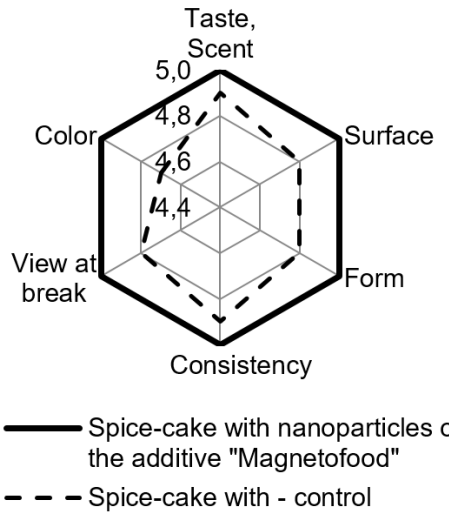

Figure 3. Levels of quality of organoleptic properties of spice-cake cooked with nanoparticles of the additive "Magnetofood" in comparison with control – spice-cake

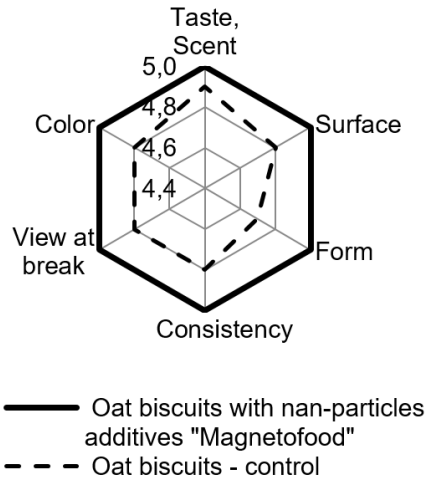

Figure 4. Levels of quality of organoleptic properties of oat biscuits with nanoparticles of the additive "Magnetofood" in comparison with the control – oat biscuits, made according to the traditional technology

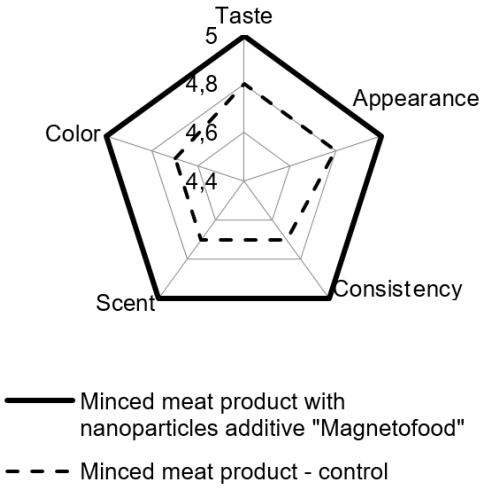

Figure 5. Levels of quality of organoleptic properties of minced meat products cut with nano-particles of additive "Magnetofood" in comparison with control – minced meat products manufactured using traditional technology

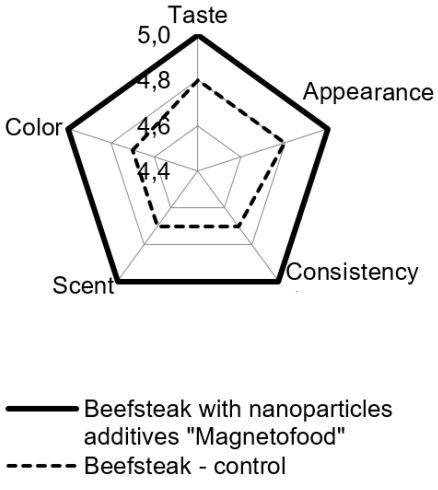

Figure 6. Levels of quality of organoleptic properties of beefsteaks with nanoparticles of supplements "Magnetofood" in comparison with control – beefsteaks made according to traditional technology

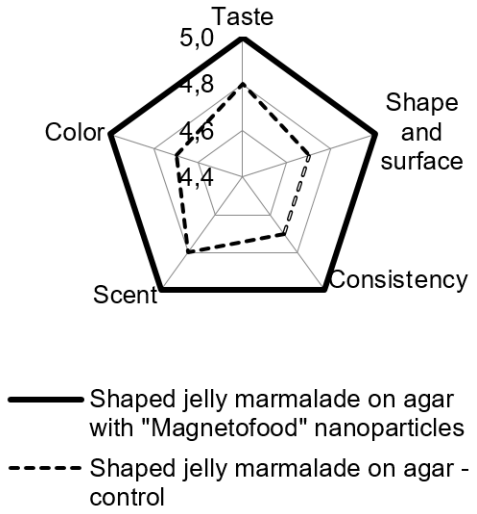

Figure 7. Levels of quality of organoleptic properties of shaped jelly marmalade with nanoparticles on agar with nanoparticles of the additive "Magnetofood" in comparison with control – shaped jelly marmalade on agar, made according to traditional technology

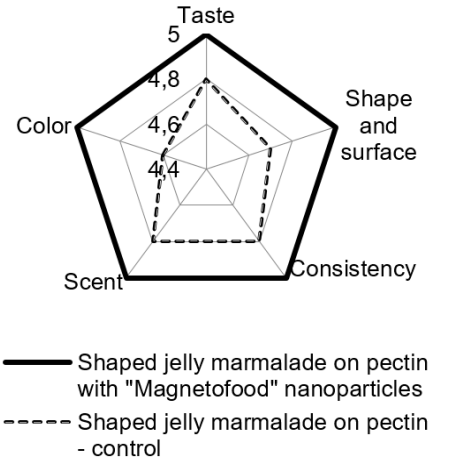

Figure 8. Levels of quality of the organoleptic properties of the shaped jelly marmalade with nanoparticles on pectin with nanoparticles of the additive "Magnetofood" in comparison with the control – shaped jelly marmalade on pectin, made according to the traditional technology

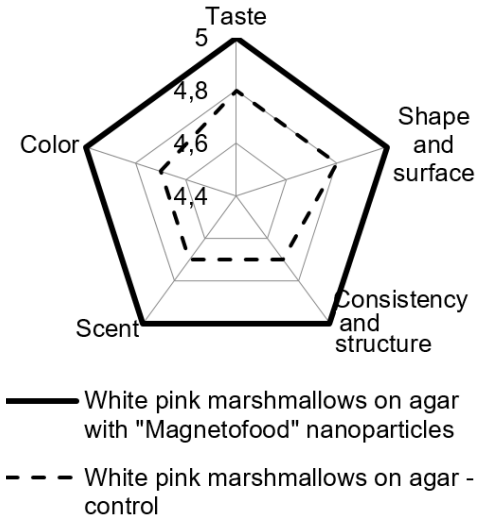

Figure 9. Levels of quality of organoleptic properties of white pink marshmallow on agar with nanoparticles of the additive "Magnetofood" in comparison with control – white and pink marshmallows on agar, made according to the traditional technology

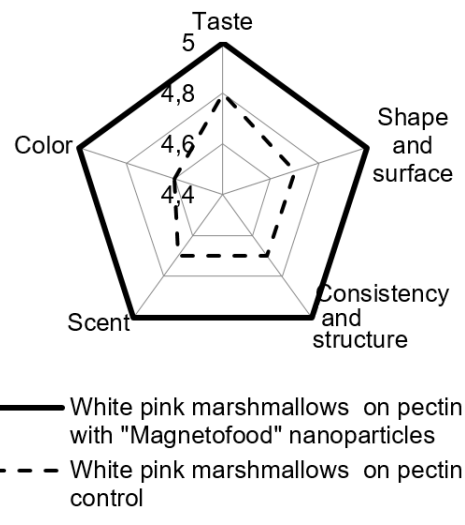

Figure 10. Levels of quality of organoleptic properties of white pink marshmallows on pectin with nano-particles of additive "Magnetofood" in comparison with control – white pink marshmallows on pectin, made according to traditional technology

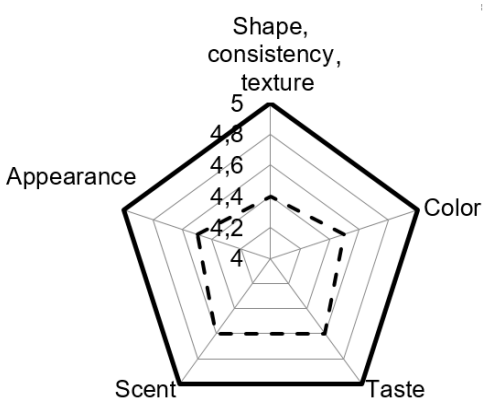

Figure 11. Levels of the quality of the organoleptic properties of the berry fruit mousse with the nanoparticles of the additive "Magnetofood" in comparison with the control – berry fruit mousse produced by traditional technology

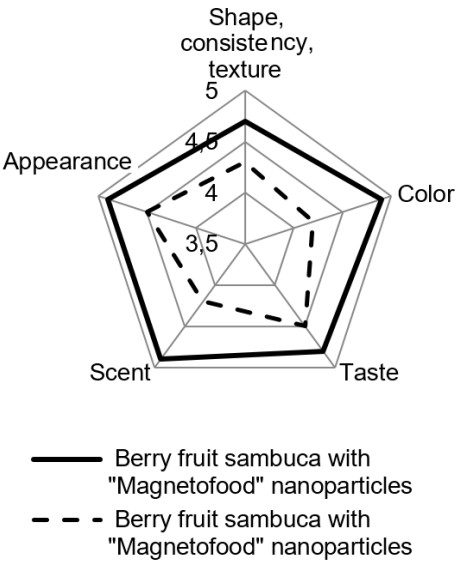

Figure 12. Levels of quality of organoleptic properties of berry fruit sambuca with nanoparticles of the additive "Magnetofood" in comparison with control – berry fruit sambuca made according to traditional technology

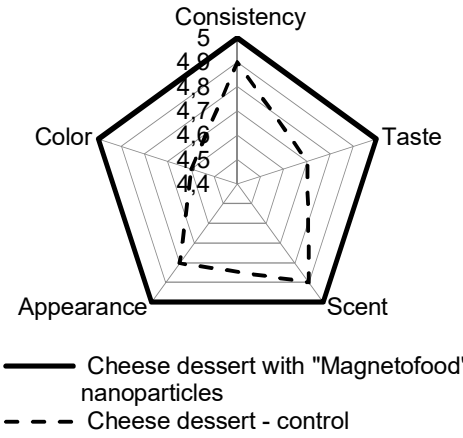

Figure 13. Levels of quality of organoleptic properties of cheese dessert with nanoparticles of supplement "Magnetofood" in comparison with control – cheese dessert made according to traditional technology

From Figure 2–13 it follows that the introduction of nanoparticles of a dietary supplement "Magnetofood" based on the two and three valence iron oxides improves the organoleptic parameters of food products by an average of 0.6–0.8 points in comparison with control samples, made according to the traditional technology. This is due to the correction of functional and technological properties of food systems under the influence of "Magnetofood" nanoparticles, in particular, stabilizing, gelling and foaming ability; the formation of aqua and lipid complexes, the uniform distribution of moisture in the system.

Table 8 shows the influence of "Magnetofood" nanoparticles on the functional and technological properties of food products.

Table 8

Output products, water-retaining ability (HRA) and fat-retaining ability (FRA) of food products with nanoparticles of food additive "Magnetofood" in comparison with control

Name of food products	Output products, %	Water-retaining ability (HRA), %	Fat-retaining ability (FRA),%
Rye – wheat bread with nanoparticles	87,9±1,0	58,0±1,0	68,4±2,0
Rye – wheat bread	82,7±1,0	50,0±1,0	62,1±2,0
Spice-cake with nanoparticles	88,7±1,0	55,0±1,0	70,4±2,0
Spice-cake «Kharkivski»	84,4±1,0	46,2±1,0	64,1±2,0
Oat biscuits with nanoparticles	86,8±0,9	56,0±1,0	69,4±2,0
Oat biscuits with traditional technology	81,4±0,9	48,0±1,0	63,1±2,0
Minced meat product with nanoparticles	85,4±0,7	82,0±0,9	73,4±1,0
Minced meat product by traditional technology	80,8±0,7	72,3±0,9	66,1±1,0
Beefsteak with nanoparticles	86,4±0,7	81,3±0,9	72,3±1,0
Beefsteaks by traditional technology	81,8±0,7	71,0±0,9	65,2±1,0

It can be seen from Table 8 that the addition of Magnetit of (Fe_3O_4) nanoparticles in the amount of 0.15% to the mass of raw materials contributes to an increase in the yield of finished products by 4.3–5.4% due to the water and fat retaining ability of the nanoparticles "Magnetofud"; HRA – by 8.0–10.3%, FRA – by 6.3–7.3% due to the mechanism of cluster affinity of nanoparticles of the additive [17, 19].

According to the expert assessments, the coefficients reflecting the quality and price availability of innovative food products are within the range of 0.67–1.0 and 0–1.0 respectively, and their ratio (quality to price) is greater than 1.0, indicating that the high value of innovative products for the consumer (Figure 14).

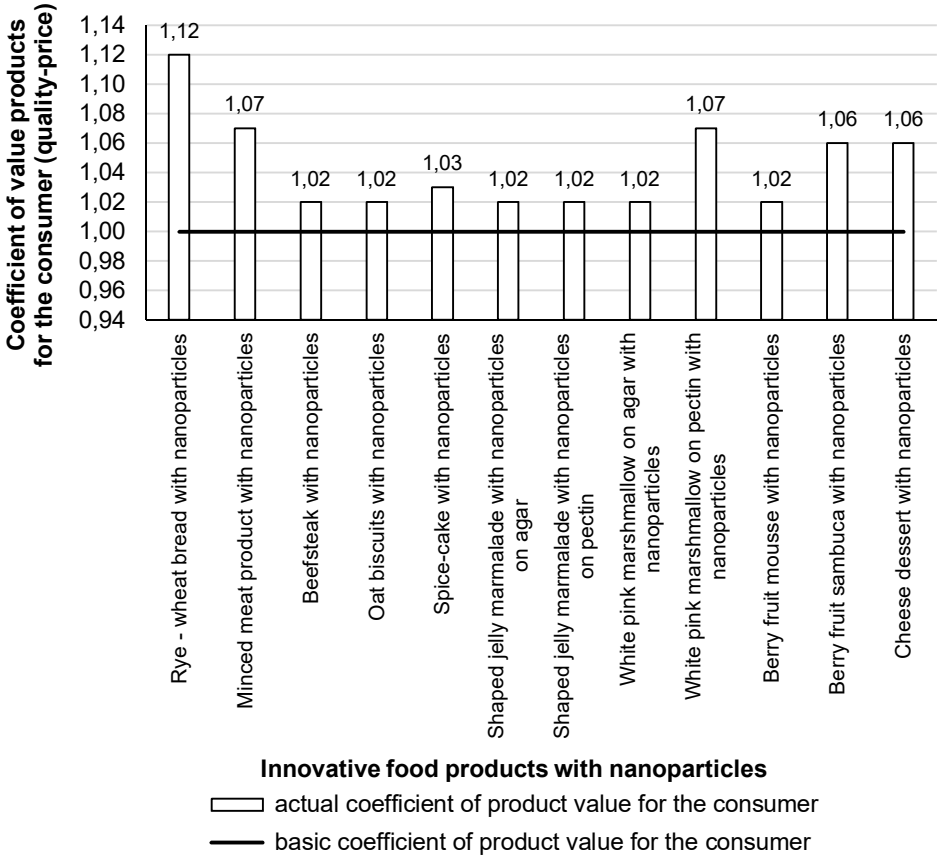

Figure 14. Indicators of the value of food products using the nanoparticles of the nutritional supplement "Magnetofood" for consumers, coefficient

The calculation of the selling prices for the new products developed and their comparison with the prices for products manufactured according to the traditional technology allowed us to conclude that as a result of the use of a nutritional supplement "Magnetofood", which causes an increase in the output of finished products, the cost of raw materials for new products are smaller compared to analogues, which, in other equal conditions, leads to an increase in profits and an increase in the profitability of products.

According to the calculations, the price of the developed innovative products corresponds to the prices for analogue products, which, taking into account higher qualitative characteristics, gives the company the opportunity to increase the profitability of innovative products by 0.2–5.4% and to obtain additional profit.

Conclusions

As a result of the study, the following conclusions were drawn.

1. Complex assessment of the effectiveness of the introduction of innovative food products had been carry out, which involves the implementation of interconnected stages in determining the scientific, scientific and technical efficiency of innovative technologies, the quality and value of innovative products for the consumer, the economic efficiency of the introduction of innovative food products.
2. The improvement of organoleptic parameters of food with the use of a food additive "Magnetofood" on the basis of on two and three valence iron oxides was improved by an average of 0.6–0.8 points in comparison with control samples, made according to the traditional technology. It was established that the addition of Magnetitofud (Fe_3O_4) nanoparticles in the amount of 0.15% to the mass of raw materials contributes to an increase in the yield of finished products by 4.3–5.4% due to the water and fat-binding properties of Magnetofood nanoparticles; HRA – by 8.0–10.3%, FRA – by 6.3–7.3% due to the mechanism of cluster affinity of nanoparticles of the additive.
3. On the basis of the integrated evaluation of innovative food products using a nutritional supplement "Magnetofood" on the basis of on two and three valence iron oxides, the effectiveness of its implementation is established.

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Анотації

Харчові технології

Характеристика ароматичних сполук і антимікробних властивостей ефірних олій з чотирьох спецій родини *Lamiaceae*

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Вступ. Представники родини *Lamiacea*е широко використовуються у харчовій промисловості, оскільки характеризуються високим вмістом ароматичних сполук.

Матеріали і методи. Оцінено хімічний склад та антибактеріальну активність ефірних олій чебрецю (Thymus vulgaris L.), розмарину (Rosmarinus officinalis L.), м'яти (Mentha spicata L.) та базиліку (Ocimum basilicum L.).

Результати і обговорення. Процентний вміст летких компонентів, отриманих методом ГХ-МС-аналізу ефірної олії чебрецю, містить тимол (37,90%) і γ-терпінен (19,44%). Визначено вміст евкаліптолу (19,89%) і камфори (16,86%) в ефірній олії розмарину та карвону (50,23%) і лимонену (13,90%) в ефірній олії м'яти. Відмінності в кількісному та якісному складі ефірних олій та їх ароматичних компонентів, якщо порівняти з попередніми дослідженнями, ймовірно, пояснюються різними екологічними та генетичними факторами, різними хіміотипами та статусом живлення рослин, а також іншими факторами, які можуть впливати на їхній склад. З'ясовано, що найбільш чутливим бактеріальним штамом є Escherichia coli. Ефірні олії м'яти і розмарину мають найбільш виражену антибактеріальну активність щодо Escherichia coli (із зонами інгібування 32 мм і 30 мм).

Висновок. Отримані результати можуть слугувати підґрунтям для поглибленого вивчення хімічного складу та антимікробних властивостей різних членів родини Lamiaceae з огляду на їх широке застосування в харчовій технології.

Ключові слова: ефірна олія, *Lamiaceae, чабрець, розмарин, м'ята, базилік.*

Кріопротекторна здатність крохмальної патоки у складі морозива ароматичного та плодово-ягідного

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Вступ. Мета наукового дослідження – вивчити вплив крохмальної патоки різного вуглеводного складу та її композиційних сумішей на формування фізико-хімічних показників морозива на основі цукрових сиропів.

Матеріали і методи. Як замінник цукру для морозива використовували крохмальний сироп з різними функціональними і технологічними властивостями – патока карамельна з низьким вмістом оцукрювання (ПК) і глюкозо-фруктозний сироп

(ГФС) з вмістом сухої речовини не менше 78%. Кріоскопічну температуру визначали за допомогою термометра Бекмана, вміст вимороженої води розраховували відповідно до одержаних значень кріоскопічної температури, мікроструктуру досліджували за допомогою світлового мікроскопу з охолоджуючою камерою за збільшення х400 та х600.

Результати і обговорення. Для повної заміни цукру у складі морозива обрано крохмальну патоку різного ступеня оцукрювання: глюкозно-фруктозний сироп ГФС (декстрозний еквівалент 98) і патоку карамельну ПК (декстрозний еквівалент 30). ГФС, порівняно з контрольними зразками з цукром, за рахунок високого вмісту моноцукрів найсуттєвіше знижує кріоскопічну температуру сумішей. Натомість ПК підвищує цей показник, тому для підтримання рекомендованого балансу за вмістом вимороженої води на кожному етапі низькотемпературного оброблення сумішей морозива доцільним є поєднання кріопротекторної здатності паток з різним декстрозним еквівалентом. Розраховані діапазони оптимальних співвідношень між ГФС і ПК у складі композиційних сумішей, що дають змогу одержувати вміст вимороженої води відповідно до контрольних зразків – від 30:70 до 40:60 для морозива ароматичного і від 50:50 до 90:10 – для морозива плодово-ягідного. Мікроструктурний аналіз зразків морозива підтвердив доцільність повної заміни цукру на композиції паток, що забезпечує формування більш гомогенної структури готового продукту, порівняно з контрольними зразками з цукром.

Висновки. Кріоскопічну температуру сумішей, вміст вимороженої води та розміри часточок дисперсних систем морозива можна регулювати шляхом застосування композицій крохмальної патоки з різним декстрозним еквівалентом.

Ключові слова: *морозиво, патока, композиція, виморожування, вода.*

Біоактивність плодів алжирської фінікової пальми *Phoenix dactylifera* L.

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Вступ. Дослідження проведено з метою оцінки *invitro* фітохімічного профілю та антибактеріальної активності плодів алжирських фінікових пальм, що відносяться до роду Phoenixdactylifera L.

Матеріали і методи. Фітохімічний аналіз якісних і кількісних (тотальних поліфенолів, флавоноїдів і антиоксидантної активності) проводили на водних і метанольних екстрактах семи сортів фініків з метою оцінки антибактеріальної активності проти штамів Staphylococcusaureus ATCC 25923 і штамів Escherichiacoli ATCC 25922.

Результати і обговорення. Фітохімічний скринінг водних і метанольних екстрактів показав наявність декількох сімейств хімічних сполук, таких як катехіновітаніни, сапоніни і терпеноїди в семи варіантах фініків. Скринінг цих екстрактів виявляє незначні якісні відмінності з перевагою сапонінів у водному екстракті, у той час як терпеноїди наявні у великій кількості в метанольному екстракті. Кількісна характеристика екстрактів показала достовірно високі рівні ($P<0,05$) в метанольному екстракті з: 85,8±0,8 до 275±0,07 мг еквіваленту галової кислоти /100 г, 36,9±0,3 до 70,1±0,9 мг еквіваленту кверцитину/100 г і 18,5±0,9 до 58,5±0,5% 66,1±0,2 до 189±0,09 мг еквіваленту галової кислоти/100g, 29,1±0,5 до 50,8±0,6 мг еквіваленту кверцитину/100 г до 14,7±0,4 до 41±0,1% у водних екстрактах для загальних

поліфенолів, флавоноїдів і знижувальної потужності відповідно. При дослідженні сприйнятливості видів бактерій до різних екстрактів плодів Phoenix dactylifera L. методом дифузії агарових свердловин визначено максимальний діаметр зони інгібування – 43,0±1,0 і 26,3±1,5 мм для метанольного екстракту сорту Tamesritпроти S. aureus і Штаму E. coli відповідно. Мінімальні інгібуючі концентрації становили від 0,08 г/мл для метанольного екстракту сорту H'miraпроти E. coli до менш ніж 0,04 г/мл для метанольних екстрактів сортів Tamesrit, Akerbouch і Bent Kbalaпроти S. aureus.

Висновок. Враховуючи вміст поліфенолів, флавоноїдів і антиоксидантну активність екстрактів фініків, можна зробити висновок, що цей продукт може бути відмінним джерелом антиоксидантів і біоконсерватів.

Ключові слова: *фінік, антибактеріальний, антиоксидант, Алжир.*

Антиоксидантні властивості та характеристики кольору бісквітного печива з функціональними компонентами

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Вступ. Досліджено вплив функціональних компонентів (топінамбур, лушпиння какао і пшениці-однозернянки) на колір, антиоксидантні та функціональні властивості бісквітних коржів.

Матеріали і методи. Антиоксидантну активність бісквітних коржів оцінювали методами ABTS, CUPRAC, FRAP і DPPH. Аналіз проб також включав вимірювання властивостей кольору в системі кольоровості CIEL*a*b* з використанням колориметра.

Результати і обговорення. Найменша антиоксидантна активність спостерігалася в 100-відсотковому пшеничному борошні (контроль), оціненому чотирма методами. Однак антиоксидантна активність не виявлена методом DPPH. Антиоксидантна активність борошна з какао-лушпинням порошку та печива з лушпинням какао досліджена чотирма методами для різних механізмів антиоксидантної дії. Антиоксидантна активність функціональних компонентів - порошок какао-лушпиння та цільнозернового борошна пшениці-однозернянки, що визначається CUPRAC-аналізом, склала 203,75±0,55 mM TE/g DM; 117,94±0,24 mM TE/g DM, а згідно з ABTS-аналізом – 107,5 ±0,68 mM TE/g DM; 520,85±5,71 mM TE/g DM відповідно.

Бісквіт з 50% цільнозернового борошна пшениці-однозернянки може розглядатися як функціональний продукт з більш ефективними антиоксидантними властивостями. Яскравість (58,50 ± 7,43), значення показників кольору a* (9,90 ± 1,93) і b* (26,31 ± 0,85) для контролю скоринки істотно не відрізнялися від показників бісквіту з цільнозернового борошна з пшениці-однозернянки (L* = 60,48 ± 6,27; a* = 9,42 ± 1,69; b * = 25,68 ± 1,44), тому що каротиноїди і лютеїн дають гарне наближення до кольору, якого надає бісквіту цільнозернове борошно із пшениці-однозернянки. Колір середини м'якуша на контрольному зразку був подібний до кольору бісквіту з цільнозернового борошна пшениці-однозернянки. Згідно з результатами, бісквіт із топінамбуром (ΔE = 6,62) та какао-лушпинням (ΔE = 23,53) має загальну різницю кольорів, яка помітна для людського ока.

Висновки. Бісквіт з цільнозерновим борошном з пшениці-однозернянки має ефективні антиоксидантні властивості. Колір контрольних зразків був подібний до кольору бісквіту із цільнозернового борошна пшениці однозернянки.

Ключові слова: *бісквіт, антиоксидант, топінамбур, какао, пшениця-однозернянка.*

Якісні показники зернових пластівців функціонального призначення

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Вступ. Обґрунтовано використання цільного біологічно активованого зерна злакових культур з метою створення функціональних харчових продуктів.

Матеріали і методи. Досліджено рецептури зернових сумішей пластівців, готові продукти на їх основі. Вміст білка визначали Біуретовим методом, вміст крохмалю – поляриметричним методом. Вміст жиру визначали методом вичерпного екстрагування хімічно чистим гексаном. Вміст вітаміну Е, речовини з Р-вітамінною активністю визначати колориметрично. Вміст вітаміну С визначали титриметричним методом. Мікробіологічні показники досліджуваних зразків визначали висіванням їх поверхнево на агаризовані поживні середовища.

Результати і обговорення. Визначено вплив температурного режиму й тривалості холодного кондиціонування зерна на його біологічну цінність. Зі зміною температурного режиму до 12–18 ºС і тривалістю кондиціювання 24–30 год вміст у зерні всіх водорозчинних вітамінів збільшується у 2–2,5 раза, кількість токоферолу зростає у 5–7 разів, кількість речовин з Р-вітамінною активністю збільшується у 2,5 раза.

Досліджено залежність основних фізико-технологічних показників зернових пластівців та органолептичних властивостей дослідних зразків готових продуктів від їх компонентного складу. Збільшення масової частки вівса до 50% зумовлює підвищення в'язкості каші внаслідок збільшення вмісту геміцелюлози, знижується розсипчастість. Підвищення масової частки зерна пшениці до 3% зумовлює більш жорстку структуру каші, що пояснюється вищою щільність оболонкових частин зерна пшениці, порівняно з іншими складовими.

Ступінь забезпечення добової потреби дорослого населення в макронутрієнтах за рахунок споживання 100 г пластівців складає: білки – 18–22%, жири – 5–7 %, вуглеводи – 13–16%, харчові волокна – 13,5%. Враховуючи добову потребу дорослого населення у вітамінах, 100 г пластівців задовольняє потребу у вітаміні Е на 67–76 %, у вітаміні Р – на 17,4 %.

Загальна кількість колонієутворювальних одиниць мезофільних аеробних і факультативно-анаеробних мікроорганізмів у свіжих зразках сумішей пластівців і після їх зберігання не перевищує $2 \cdot 10^3$ на г продукту, плісняві гриби та патогенні мікроорганізми відсутні.

Висновки. Біологічно активоване зерно злакових культур пшениці, голозерного вівса й тритикале є джерелом цінних нутрієнтів для створення сумішей пластівців функціонального призначення.

Ключові слова: *активування, пшениця, тритикале, овес, пластівці.*

Вплив високого тиску та додавання ізоляту соєвого білка на вологоутримувальну здатність і текстуру свинячого фаршу

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Вступ. Обробка високим тиском і додавання ізоляту соєвого білка до свинячого фаршу може покращити його якість, вологоутримувальну здатність, текстуру та збільшити вихід готового продукту.

Матеріали і методи. Зразки фаршу містили: С1 – 2400 г м'яса свинини, 80 г тушкової свинини, 70 г води з льодом, 10 г NaCl; зразок С2 додатково містив10 г ізоляту соєвого білка (2%); зразок С3 – 20г соєвого білкового ізоляту (4%). Сирий фарш пакували під вакуумом і обробляли тиском 200 МПа протягом 10 хв при 10 ± 2 °С. Вимірювання релаксації ЯМР низького поля проводили згідно з ЯМР-зондом імпульсного ЯМР-аналізатора Niumag.

Результати і обговорення. Якщо порівняти зі зразком С1, показник виходу продукту зі зразків С1 і С2 значно збільшився. Емульгуюча дія 11S-глобулінів покращилася при тиску 200 МПа, що збільшило водоутримувальну здатність ізоляту соєвого білка. При цьому показники твердості, пружності, когезії і розжовуваності зразків С2 та С3 значно збільшилися, за винятком показника пружності в зразку С3. Якщо порівняти зі зразком С3, показники твердості, пружності, когезії і розжовуваності у зразку С2 значно збільшилися. Обробка продукту тиском понад 200 МПа спричиняє денатурацію і/або агрегацію білка, що обмежує його функціональні властивості. Використання ЯМР у слабкому полі дало змогу визначити три характерних граничних співвідношення виробів, приготованих з свинячого фаршу. Вироби, виготовлені з свинячого фаршу з вмістом різної кількості ізоляту соєвого білка, мали щільну консистенцію через зміни білка, який швидко релаксує, і протонів води, які релаксують повільно. Емульгуюча дія 11S-глобулінів значно покращилася при тиску 200 МПа завдяки змінам розчинності білка, гідрофобності поверхні, вмісту вільної сульфгідрильної групи і вторинної структури.

Висновки. Вплив комбінації високого тиску і різного вмісту ізоляту соєвого білка на гелеві властивості виробів, приготованих з свинячого фаршу, має значні відмінності. Якщо порівняти зі зразком С1, то зразки С2 і С3 характеризувалися більш високим виходом продукту, і жорсткістю, цілісністю і разжовуваністю; зразок С2 мав кращу водоутримувальну здатність і консистенцію.

Ключові слова: *тиск, ізолят, соя, білок, вологоутримування, текстура, ЯМР.*

Визначення терміну зберігання маринованого копченого морського окуня в умовах охолодження

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Вступ. Для дослідження якості за органолептичними, хімічними та мікробіологічними показниками і термінів зберігання були підготовлені два різних маринади (звичайний і копчений) з морським окунем.

Матеріали і методи. Риба, що постачається з аквакультурного закладу, була доставлена в лабораторію за умов холодного зберігання і очищена до філе. Першу групу (група А: звичайна) вводили в маринований розчин (співвідношення риба: розчин – 1: 2, 1,68% спиртового оцту, 6,4% солі і 0,01% лимонної кислоти) протягом 5 днів. У другій групі (група В: копчена) рибу коптили і повітря охолоджували до температури навколишнього середовища. У маринаді холодні рибні філе (співвідношення риба: розчин – 1:2, 1,2% спиртового оцту, 5,5% солі та 0,01% лимонної кислоти) знаходилися протягом 2 днів.

Результати і обговорення. За результатами хімічних аналізів було визначено значення ТВА – 0,26±0,01 mgMDA/kg у сировині. У кінці дослідження ця величина склала 4,38±0,05 mgMDA/kg у групі А (5-й місяць) і 3,05±0,02 mgMDA/kg у групі В (7-й місяць). За результатами мікробіологічних аналізів кількість МАФАМ становила 2,00±0,04 CFU/g у сировині, але загальна кількість бактерій і дріжджових грибів була меншою 10 CFU/g протягом періоду зберігання. У процесі дослідженні бактерії коліформи (БГКП) не виявлені. аналізу П'ять досвідчених експертів оцінили органолептичні показники продукції (колір, запах, текстуру, смак). Обидві групи отримали високі оцінки на початку, але група А отримала низькі оцінки в 5-у місяці зберігання, а група В мала низькі бали на 7-у місяці і втратила якість.

Висновок. У результаті маринад копченого морського окуня був оцінений вище, ніж звичайний, до того ж, термін зберігання маринаду копченого морського окуня був довшим, ніж звичайного.

Ключові слова: *морський окунь, копчення, якість, маринування.*

Використання клиноптилоліту, активного вугілля та гірського кришталю в технології підготовки води для підвищення біологічної цінності хлібного квасу

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Вступ. Визначено вплив підготовленої за допомогою клиноптилоліту, гірського кришталю та активного вугілля водопровідної питної води на вітамінний склад сусла і квасу.

Матеріали і методи. Аналізували квас, який отримували шляхом ферментації квасного сусла на житній основі дріжджами Saccharomyces cerevisiae МП-10. Сухі речовини визначали ареометричним методом, вміст вітамінів за здатністю тест-культур рости за наявності певних вітамінів. Тіамін та рибофлавін визначали флуорометричним методом.

Результати і обговорення. У підготовленій воді вміст загального заліза становив 0,01 мг/дм^3, загальна жорсткість – 1,1 ммоль/дм^3, перманганатна окиснюваність – 0,5 мг O_2/дм^3. Характер бродіння був схожим для обох зразків. При цьому загальна тривалість бродіння дослідного зразка була на 13% меншою, що пояснюється зниженням кількості вітамінів у вихідному суслі. Мінеральний склад води суттєво впливав на вміст вітамінів у вихідному та зброджeному суслі і квасі, зокрема кількість тіаміну і рибофлавіну у дослідних зразках збільшувався в середньому у 2,5 раза, вміст фолієвої кислоти у 5 разів, що можна пояснити утворенням в контрольному зразку нерозчинних у воді комплексів з двовалентними металами. При використанні модельних розчинів із показником загальної жорсткості 5 ммоль/дм^3 вміст тіаміну в

збродженому суслі знизився в 6,7 раза, якщо порівняти із суслом на демінералізованій воді. Для забезпечення високого вмісту вітамінів у квасі, зокрема тіаміну, рибофлавіну та фолієвої кислоти технологічна вода повинна мати загальну жорсткість не більше 1 ммоль/дм^3 і не містити іонів заліза.

Висновки. Використання підготовленої води забезпечує збільшення вмісту вітамінів у квасі та отримання продукту із прийнятним для фізіологічних потреб організму людини співвідношенням.

Ключові слова: *вода, водопідготовка, сусло, квас, вітамін.*

Процеси і обладнання

Визначення параметрів систем рекуперації теплових потенціалів потоків газопарових сумішей

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Вступ. Стаття стосується визначення співвідношень енергетичних потенціалів у масових потоках газових і парогазових систем, їх змін у термодинамічних перетвореннях і можливостей регенерації.

Матеріали і методи. Теоретичне феноменологічне дослідження на основі законів термодинаміки, матеріальних і енергетичних балансів та закономірностей синтезу систем із рекуперацією теплової енергії.

Результати і обговорення. Спалювання вхідних газових потоків, що використовуються як першоджерела хімічних енергетичних потенціалів з перетворенням у теплову енергію, супроводжуються втратами на рівні теплоти конденсації утвореної парової фази. Парогазові суміші генеруються в процесах сушіння, аерації зернових масивів за пророщування, в системах аеробних процесів бродіння, за аерації промислових стоків тощо.

Перебіг таких процесів відбувається за термодинамічних параметрів, які не відповідають аналогічним характеристикам навколишнього середовища, що супроводжується енергетичними втратами на рівнях різниці їхніх ентальпій. З цієї точки зору важливою складовою таких газопарових сумішей є парова фракція води, оскільки вона несе в собі тепловий потенціал пароутворення.

У статті визначено співвідношення параметрів матеріальних і теплових потоків, з'ясовано, що енергетичний потенціал конденсації парової фази в продуктах горіння газів близький до 10% їхньої теплотворної здатності.

Виконано оцінку перспектив застосування теплових труб у системах рекуперації теплових потоків за рахунок створення замкнутих енергетичних контурів. Показано можливість поєднання ними теплообмінних поверхонь охолодження і нагрівання тепловими трубами, за якого досягаються однакові показники температури випаровування і конденсації проміжних теплових агентів, наведено термодинамічні параметри останніх з точки зору можливості їх застосування в створюваних системах.

Висновки. Теплові труби в запропонованих системах дають змогу досягати однакових показників температур випаровування та конденсації теплових агентів, а наявність як перетворювачів тисків компресорів і детандерів перетворює системи в локальні теплові насоси.

Ключові слова: *рекуперація, тепловий потенціал, тепловий насос.*

Моделювання режимів погіршення тепловіддачі під час концентрування розчинів у промислових плівкових випарних апаратах

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Вступ. Погіршення тепловіддачі під час концентрування густих цукрових розчинів у плівкових випарних апаратах відбувається без утворення ривулет ті порушення цілісності плівки.

Матеріали і методи. Фізичне моделювання теплогідродинамічних характеристик кільцевих низхідних пароріднних потоків висококонцентрованих цукрових розчинів виконано в трубі довжиною 9 м діаметром 30 мм, поділеної на 20 ділянок для дискретного вимірювання теплового потоку, концентрації розчину й температури стінки труби.

Результати і обговорення. Математичне моделювання концентраційного й температурного полів у стікаючій плівці густого цукрового розчину під час випаровування на основі рівнянь конвективної дифузії та теплопровідності з параболічним профілем швидкості в плівці показує, що відповідність експериментальним даним щодо темпу падіння теплового потоку вздовж випаровувального каналу має місце лише за умови врахування періодичного перемішування плівки великими хвилями (напливами). Режим погіршення тепловіддачі надається як взаємодія циклічних процесів наростання концентрації на міжфазній поверхні з відповідним зростанням температурної депресії під час міжхвильової паузи, та періодичним вирівнюванням концентрації з порушенням упорядкованої структури плівки під час проходження великої хвилі (напливу). Аналітичні вирази для розрахунку процесів зростання міжфазної концентрації та падіння теплового потоку надаються в межах хвильового циклу, а відтворення розвитку кризового падіння теплового потоку вздовж усього каналу здійснюється дискретно з кроком, що відповідає довжині великих хвиль.

Експериментально не виявлено кризової стрибкоподібної зміни теплового потоку по довжині труби, а лише пришвидшення темпу падіння, починаючи з концентрації від 75% і вище. Числа Прандтля змінювалась в межах 35–250 по довжині труби в процесі падіння теплового потоку. Рекомендовані співвідношення для розрахунку коефіцієнта тепловіддачі дійсні у діапазоні 3–15 кВт/м^2 та 0,05–0,3 кг/м с масової щільності зрошення. Найбільше відхилення розрахованих даних від отриманих експериментально складає на більше 15%.

Висновок. Модель періодичного руйнування поверхневого прошарку плівки з надвисокою концентрацією великими хвилями адекватно відображає процеси погіршення тепловіддачі до густих плівок.

Ключові слова: *плівка, випаровування, теплообмін, концентрування.*

Моделювання гідродинамічних умов при обробленні рідких систем знакозмінними імпульсами тиску

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Вступ. Метою цієї наукової статті є дослідження впливу застосування знакозмінних імпульсів тиску під час оброблення рідких систем шляхом проведення чисельного моделювання.

Матеріали і методи. Використовувались методи тривимірного об'ємного параметричного імітаційного моделювання та візуалізації, математичне моделювання умов, які виникають в робочій частині роторно-пульсаційних апаратів під час оброблення рідких систем. Експериментальні дослідження одержаних і контрольних рідких зразків проводились з використанням потенціометричного лабораторного вимірювального обладнання.

Результати і обговорення. Встановлено, що величини локальних значень тисків у зоні проходження робочих органів роторно-пульсаційного апарата водними розчинами становлять: біля зовнішньої поверхні внутрішнього ротора – від -50 до +300 кПа; біля зовнішньої поверхні статора – від -150 до 100 кПа; біля внутрішньої поверхні статора – від +40 до -120 кПа; біля внутрішньої поверхні зовнішнього ротора – від + 100 до -100кПа. При останніх значеннях визначається зона, в якій може за певних умов реалізовуватись кавітація та адіабатичне закипання. Під час оброблення води та водних розчинів, а також процесу змішування водних розчинів в умовах гідродинамічних осциляцій, а саме: знакозмінних імпульсів тиску, величини зміни тиску характеризуються: ΔP = 350 kPa біля зовнішньої поверхні внутрішнього ротора; ΔP = 250 kPa біля зовнішньої поверхні статора; ΔP = 160 kPa біля внутрішньої поверхні статора; ΔP = 200 kPa біля внутрішньої поверхні зовнішнього ротора.

При проведенні чисельного експерименту враховувались конструктивні та геометричні параметри роторно-пульсаційних апаратів. Найбільшого значення величина швидкості зсуву потоку набуває при кільцевих коаксіальних зазорах у 100 мкм. За результатами розрахунку було встановлено, що найбільші напруження зсуву виникають у РПА з кільцевими коаксіальними зазорами 100мкм.

Були обраховані поля тисків, що виникають при роздільному введенні компонентів до робочої зони РПА, які надають можливість впливати на зміну фізико-хімічних параметрів рідких систем.

Висновки. Визначені величини зміни тиску в робочій камері роторно-пульсаційного апарата при проходженні системи «ротор-статор-ротор». Використання цих величин дає змогу одержувати рідини з необхідними заданими фізико-хімічними параметрами та керувати цим процесом.

Ключові слова: *вода, тиск, гідродинамічний, імпульс, знакозмінний.*

Моделювання процесу замішування дріжджового тіста кулачковими робочими елементами

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Вступ. Сформульовано математичну модель та проведено імітаційне моделювання процесу замішування дріжджового тіста кулачковими робочими елементами.

Матеріали і методи. На етапі формування задачі задаються умови контактної взаємодії матеріалу з робочими елементами та камерою замішування, а також значення структурно-механічних характеристик тіста. Під час моделювання процесу замішування змінювали кут розташування кулачкового елемента від 90° до 585°.

Результати і обговорення. Розроблена схема математичного моделювання процесу замішування дріжджового тіста в тістомісильній машині безперервної дії. На основі результатів імітаційного моделювання процесу замішування кулачковими робочими елементами отримано розподілення напруження зсуву та дисипації дріжджового тіста в робочій камері. Зі збільшенням кута розташування (від 90° до 360°) кулачкового елемента на валу відбувається підвищення напруження зсуву. Найбільші показники напруження зсуву відбуваються в зоні зачеплення кулачкових робочих елементів та в зоні контакту кулачків зі стінками корпусу, числові значення сягають 7000-8000 Па. По решті камери замішування напруження зсуву сягає 1000-3000 Па. Розподілення дисипації показує, що в частинах робочої камери відбувається утворення тепла в області течії. Зі збільшенням кута розташування (від 180° до 585°) кулачкового елемента відбувається поступове підвищення температури. На ділянці замішування в зоні 12 пари кулачків температура дріжджового тіста збільшується майже на 5°С. Враховуючи, що перед початком моделювання початкова температура сягала t=30°С, а після завершення процесу замішування не перевищувала 35°С, параметри тістоготування дотримані. Найбільше виділення тепла відбувається на ділянці зачеплення кулачкових робочих елементів.

Результати математичного моделювання підтверджені фізичними експериментами на дослідній тістомісильній машині безперервної дії, похибка в межах 5%.

Висновки. Запропонована схема моделювання дає змогу досліджувати процес замішування дріжджового тіста за різних технологічних параметрів. Отримані результати забезпечують вихідні дані для вибору раціональних параметрів процесу замішування дріжджового тіста кулачковими робочими елементами.

Ключові слова: *моделювання, замішування, тісто, кулачки, імітація.*

Економіка і управління

Вплив витрат на страхування на конкурентоспроможність підприємств харчової промисловості в контексті безпеки продовольчого ринку

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Вступ. Метою статті є аналіз витрат на страхування та дослідження загальних тенденцій, особливостей і впливу витрат на страхування на конкурентоспроможність підприємств харчової промисловості в контексті безпеки продовольчого ринку.

Матеріали і методи. Теоретичним обґрунтуванням статті був науковий літературний огляд проблем витрат на страхування, безпеки на продовольчому ринку та конкурентоспроможності. Використано методи порівняння, статистичний аналіз даних, систематизація, узагальнення та порівняння показників частки ринку і ємності, рентабельності, ефективності, витрат на страхування, а також метод кореляційно-регресійного аналізу та його показники.

Результати і обговорення. Досліджувані підприємства харчової промисловості не порушують норми чинного антимонопольного законодавства України. Найбільші значення всіх трьох видів рентабельності були характерні для ПАТ «Карлсберг Україна». Визначено темпи зміни витрат на страхування для вибраного переліку підприємств харчової промисловості. Результати показують широкий інтервал зміни цих показників за 2014-2015 роки: від -99,6 % (ПАТ «Дім марочних коньяків «Таврія») до 881,4 % (ПАТ «Пологівський олійноекстракційний завод»). У результаті дослідження встановлено, що найбільша частка витрат зафіксована у 2016 році для ПАТ «Пологівський олійноекстракційний завод» – на рівні 2,173%. Отже, витрати на страхування несуттєво змінюють витрати і, відповідно, помірно впливають на формування прибутку підприємств харчової промисловості.

Науковий аналіз свідчить про пряму пропорційну залежність між ROE і витратами на страхування для ПАТ «Карлсберг Україна», обернену пропорційність між ROS і витратами на страхування для ПАТ «Оболонь» і ПрАТ «Київська кондитерська фабрика «Рошен».

Кореляційно-регресійний аналіз показників рентабельності та витрат на страхування для підприємств харчової промисловості показує, що тільки три коефіцієнти детермінації r^2 відповідають значенням регресійної моделі задовільної якості: r^2=0,717 (*ROE*, ПАТ «Карлсберг Україна»); r^2=0,838 (*ROS*, ПАТ «Оболонь»); r^2=0,664 (*ROS*, ПрАТ «Київська кондитерська фабрика «Рошен»). Менші значення (проміжок r^2 в інтервалі 0,1–0,5) коефіцієнта детермінації зафіксовані у дев'яті випадках: в межах від мінімального значення r^2=0,103 для показника *ROS* для ПАТ «Пологівський олійноекстракційний завод» до максимального r^2=0,496 для показника *ROE* для ПАТ «Київхліб».

Висновки. Гіпотеза про існування залежності між конкурентоспроможністю ПХП та частиною грошей, що виділяється ПХП на страхування може мати підтвердження лише для ПХП з високою ефективністю ведення бізнесу.

Ключові слова: *страхування, витрати, харчова промисловість, конкурентоспроможність.*

Взаємозв'язок якісного і кількісного рівнів доступності та достатності харчування при визначенні рівня продовольчої безпеки

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Вступ. Для якісного і повноцінного аналізу продовольчої безпеки необхідний набір показників, які забезпечують якісний і кількісний підхід для оцінювання продовольчої доступності та достатності.

Матеріали і методи. Об'єктом досліджень є аналіз продовольчої безпеки та індикатори продовольчої доступності і достатності, за допомогою яких він здійснюється. В процесі дослідження використовувались методи статистичного аналізу в частині побудови трендів питомої ваги витрат на продукти харчування в сукупних витратах домогосподарств за 2000-2017 роки із визначенням його аналітичного рівняння й вартості одиниці енергії добового раціону харчування і споживчих цін в Україні.

Результати і обговорення. Для оцінки фізичної доступності використовуються норми верхньої межи раціонального або оптимального харчування, норми мінімального продовольчого споживання, калорійність харчового раціону людини, відсоток забезпечення калорійності добового раціону за рахунок споживання продуктів тваринного походження. Для оцінки економічної доступності: рівень цін на продукти харчування, питома вага витрат на продукти харчування в сукупних витратах домогосподарств, коефіцієнти диференціації харчування за соціальними групами. Вони не відображають повною мірою стан продовольчої доступності. Для оцінки продовольчої доступності пропонується використовувати показники купівельної спроможності 1 ккал, який визначається як відношення кількості ккал енергії добового раціону харчування середньостатистичного українця до питомої ваги витрат на харчування в загальному обсязі сукупних витрат домогосподарств, і вартість одиниці енергії добового раціону харчування із порівнянням з індексом споживчих цін. Так, проведені розрахунки показали, що в Україні у 2000 році на 1% витрат на харчування в бюджеті сукупних витрат домогосподарств припадало 41 ккал, у 2017 році – 52,5, що складає 28% від рівня 2000 року. Отже, доступність харчування у 2017 році покращилася порівняно із 2000 роком. Також досліджувались темпи зростання вартості 1 тис. ккал, які у 2000–2014 і у 2017 роках випереджали темпи зростання споживчих цін. Це є свідченням того, що в ці періоди продовольчу доступність формує не ціна, , а рівень доходів, особливо в частині витрат на харчування.

Висновки. Комплексне використання цих показників дасть змогу більш повно оцінити рівень продовольчої доступності населення і розробити заходи вчасного запобігання виявлених загроз.

Ключові слова: *продовольство, безпека, доступність, достатність.*

Комплексний аналіз ефективності харчової продукції з використанням наночастинок харчової добавки на основі оксидів дво- та тривалентного заліза “Магнетофуд”

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Вступ. Впровадження нанотехнологій у виробництво харчової продукції є одним із чинників забезпечення стійких конкурентних переваг підприємств харчової галузі. Представлено комплексний аналіз оцінки ефективності нової харчової продукції з використанням наноночастинок харчової добавки на основі оксидів дво- та тривалентного заліза «Магнетофуд».

Матеріали і методи. Харчова продукція, вироблена з використанням наночастинок оксидів дво- та тривалентного заліза «Магнетофуд» (Fe_3O_4), досліджувалася з використанням стандартних і загальноприйнятих методів експериментальних досліджень (органолептичних показників за 5-бальною шкалою; волого- та жироутримувальної здатності за допомогою жироміра та рефрактометра; виходу готового продукту за різницею мас), експертного аналізу.

Результати і обговорення. Проведені дослідження свідчать, що впровадження науково обґрунтованої харчової продукції з наночастинками дасть змогу виробляти конкурентоспроможну продукцію. Харчова добавка «Магнетофуд» має значний функціонально-технологічний потенціал (сорбційні, антиоксидантні, бактеріостатичні, емульгуючі, стабілізуючі, піно- і драглеутворюючі, водо- і жирозв’язуючі, водо- та жироутримувальні властивості), що обумовлює внесення наночастинок добавки до рецептур хлібобулочних, борошняних кондитерських, м’ясних, пастильно-мармеладних виробів та сиркових і збитих десертів. Це сприяє ресурсозбереженню під час виробництва харчової продукції, формуванню високих споживчих властивостей, підвищенню виходу й економічної ефективності її виробництва. Харчова продукція, виготовлена з використанням харчової нанодобавки «Магнетофуд», має високі органолептичні, функціонально-технологічні властивості, подовжений термін зберігання. За результатами порівняльного аналізу якісних і цінових характеристик харчової продукції з наночастинками «Магнетофуд» зроблено висновок про більшу цінність нових продуктів для споживачів B2C порівняно з продуктами-аналогами.

Висновки. Доведено високий рівень наукової, науково-технічної, соціальної та економічної ефективності продуктів харчування з додаванням харчової добавки на основі оксидів дво- та тривалентного заліза «Магнетофуд».

Ключові слова: *інновація, наночастинки, магнетофуд, якість.*

Instructions for authors

Dear colleagues!

The Editorial Board of scientific periodical
"**Ukrainian Food Journal**"
invites you for publication of your research results.

Requirements to all texts:
Language – English.
Size of the article – 10–15 pages in Microsoft Word 2003 and earlier versions with filename extension *.doc (!)
Times New Roman, font size 14, 1 line intervals, margins on both sides – 2 cm.

The structure of the article:

1. The title of the article
2. Authors (full name and surname)
3. Institution, where the work has been performed.
4. Abstract (2/3 of a page). The structure of the abstract should correspond to the structure of the article (Introduction, Materials and methods, Results and discussion, Conclusion).
5. Keywords.
6. The main body of the article should contain the following parts:
   - Introduction
   - Materials and methods
   - Results and discussion
   - Conclusion
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   If you need you can add another parts and/or divide them into subparts.
7. The information about the author (Name, surname, scientific degree, place of work, email and contact phone number).

All figures should be made in graphic editor, the font size 14.

The background of the graphs and charts should be only in white color. The color of the figure elements (lines, grid, text) – in black color.
Figures and EXCEL format files with graphs additionally should be submitted in separate files.
Photos are not recommended to be used as graphical materials.

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Шановні колеги!

Редакційна колегія наукового періодичного видання «**Ukrainian Food Journal**» запрошує Вас до публікації результатів наукових досліджень.

Вимоги до оформлення статей

Мова статей – англійська.

Мінімальний обсяг статті – **8 сторінок** формату А4 (без врахування анотацій і списку літератури)**.**

Стаття виконується в текстовому редакторі Microsoft Word 2003, в форматі *.doc.

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

Всі поля сторінки – по 2 см.

Структура статті:

1**.** УДК**.**
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4. *Установа, в якій виконана робота.*
5. Анотація. **Обов’язкова** структура анотації:
   - Вступ (2–3 рядки).
   - Матеріали та методи (до 5 рядків)
   - Результати та обговорення (пів сторінки).
   - Висновки (2–3 рядки).
6. Ключові слова (3–5 слів, але не словосполучень).

Пункти 2–6 виконати англійською і українською мовами.

7. Основний текст статті. Має включати такі обов’язкові розділи:
   - Вступ
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За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

8. Авторська довідка (Прізвище, ім’я та по батькові, вчений ступінь та звання, місце роботи, електронна адреса або телефон).
9. Контактні дані автора, до якого за необхідності буде звертатись редакція журналу.

Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним** (!) тексту статті. **Фотографії можна використовувати лише за їх значної наукової цінності.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

Рисунки та графіки EXCEL з графіками додатково подаються в окремих файлах.

Скорочені назви фізичних величин в тексті та на графіках позначаються латинськими літерами відповідно до системи СІ.

В списку літератури повинні переважати англомовні статті та монографії, які опубліковані після 2000 року.

Правила оформлення списку літератури

В Ukrainian Food Journalвзято за основу загальноприйняте в світі спрощене оформлення списку літератури згідно стандарту Garvard. Всі елементи посилання розділяються **лише комами**.

1. Посилання на статтю:

Автори А.А. (рік видання), Назва статті, Назва журналу (курсивом), Том (номер), сторінки.

Ініціали пишуться після прізвища.

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1. Приклад:
   Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (Juglans regia L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies,* 2(2), pp. 104–108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

Приклад:

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

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Приклади:

1. (2013), *Svitovi naukovometrychni bazy*, available at: http://www1.nas.gov.ua/publications/q_a /Pages/scopus.aspx
2. Cheung T. (2011), *World's 50 most delicious drinks [Text]*, Available at: http://travel.cnn.com/explorations/drink/worlds–50-most-delicious-drinks–883542

Список літератури оформлюється лише латиницею. Елементи списку українською та російською мовою потрібно транслітерувати. Для транслітерації з українською мови використовується паспортний стандарт, а з російської – стандарт МВД (в цих стандартах використовуються символи лише англійського алфавіту, без хвостиків, апострофів та ін).

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Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

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