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Effect of methyl jasmonate, salicylic acid and ascorbic acid on quality parameters of strawberry (*Fragaria x ananassa* Duch) fruit during cold storage

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Abstract

Keywords:

Strawberry
Phenolic
Antioxidant
Anthocyanins
Methyl jasmonate
Salicylic acid,
Ascorbic acid

Introduction. The objective of this work was to investigate the combined solution effects of methyl jasmonate, salicylic acid and ascorbic acid on storability of strawberry fruits.

Materials and methods. The anthocyanins were quantified by the pH differential method. Total phenolic compounds were determined by method using Folin-Ciocalteu reagent. FRAP assay was applied in order to determine antioxidant activity. Determination of individual anthocyanins by HPLC was performed by a Varian- Prostar-500 series liquid chromatograph. The texture analyses of the strawberries were carried out using a Texture Analyser.

Results and discussion. Effect of combined solution of Methyl jasmonate (MJ), Salicylic acid (SA) and Ascorbic acid (AA) on storability of strawberry fruits (Victoria and Camarosa varieties) was investigated. Treatment with MJ, SA and AA positively influenced on the level of content of vitamin C in strawberries fruits during storage. Total anthocyanins in the control samples of Victoria gradually decreased from 21.35 ± 1.06 to 13.35 ± 0.66 $\text{mg}100\text{g}^{-1}$ on the 13-th day of storage. As to the treated samples, anthocyanins content reduced to 15.49 ± 0.77 $\text{mg}100\text{g}^{-1}$. In the samples of Camarosa total anthocyanins reduced from 46.93 ± 2.34 to 20.41 ± 1.02 and to 34.59 ± 1.72 mg per 100 g fruits in control and treated samples respectively. Total phenolic compounds (TPC) in the control samples of Victoria initially was equal to 129.86 ± 6.49 $\text{mg}100\text{g}^{-1}$ and at the end of experiment, it reduced to 111.15 ± 5.55 $\text{mg}100\text{g}^{-1}$. Whereas, in the treated sample TPC was unchanged. TPC in Camarosa initially was by 40% more than in Victoria, i.e. 181.51 ± 9.07 $\text{mg}100\text{g}^{-1}$. After 13 days of storage, TPC reduced to 131.00 ± 6.55 and to 150.02 ± 7.50 $\text{mg}100\text{g}^{-1}$ in the control and treated samples respectively. Effect of treatment was statistically and practically significant. During storage period, antioxidant activity of the fruits decreased gradually. Change in antioxidant activity of the treated samples was less significant than in untreated sample. i.e by 17.9 and 23.3 % for the fruits of Victoria and Camarosa varieties respectively. Main anthocyanin in the fruits of both varieties was Pelargonidin-3-O-glucoside. Its initial content in the fruits was 68.45 ± 3.42 and 65.28 ± 3.26 % of total anthocyanins for Victoria and Camarosa varieties respectively.

Conclusion Treatment of fruits of strawberry with combined solutions of methyl jasmonate, salicylic acid and ascorbic acid positively influenced on storability of the fruits. Maintenance of anthocyanins and total phenolics as well as antioxidant potential during storage period was statistically significantly increased. Treatment with combined solution resulted in improvement of texture of fruits during storage process.

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Introduction

Strawberries (*Fragaria x ananassa* Duch) are one of the most popular berries in the world. The quality, chemical composition and sensory parameters of strawberries during fresh storage period have been studied intensively [1]. Strawberries are a good source of vitamins and minerals, and their quality and chemical composition vary among cultivars and with postharvest handling conditions [2]. Also, strawberry fruit is a rich source of natural antioxidants and phytochemicals, particularly anthocyanins, flavonoids, phenolic acids [3-8]. However, shelf life of strawberries is very limited. During fresh storage fruits undergo significant microbial decay, fruit softening, water loss, loss of red color, brown pigment formation, and flavor changes [1, 9–10].

Various chemical compounds have been used to treat the strawberry fruits in order to reduce such undesirable changes during storage period and to prolong shelf life of the fruits.

MJ and SA are endogenous plant hormones that play principal roles in regulating stress responses and plant development [11–12].

Methyl jasmonate (MJ) is a plant growth regulator and it very actively participates in many physiological processes [12, 13]. MJ serves as a signal molecule to initiate the defense mechanism in response to stress conditions [14]. According to Cardemil and co-authors, post-harvest treatments of fruits with jasmonate stimulates the production of such antioxidants as flavonoids, anthocyanins, phenolic acids; improve the fruits quality and prolongs their shelf life [15].

Salicylic acid (SA) is a hormonal substance, participating in regulation of numerous physiological processes [16]. SA can inhibit biosynthesis of ethylene in fruits and in such a way delay the ripening of fruits. SA reduces fruit deterioration caused by chill injury and fungal disease during fresh storage period [17].

Ascorbic acid (AA) is known to inhibit browning process in fruits. In addition, AA is cheap and safe for human consumption [18, 19–24].

The objective of our work was to investigate the combined solution effects of methyl jasmonate, salicylic acid and ascorbic acid on storability of strawberry fruits.

Material and methods

2.1 Chemicals

Ascorbic acid higher than 99.0% and potassium dihydrogen phosphate were purchased from Sigma-Aldrich (Steinheim, Germany); TPTZ – 2-4-6-tris (2-pyridyl)-s-triazine (Sigma-Aldrich, Switzerland), the Folin-Ciocalteu reagent (Appli Chem, Germany), hydrochloric acid, formic acid and phosphoric acid were provided by Merck (Darmstadt, Germany); sodium carbonate was purchased from ChemCruz (ChemCruz Biochemicals, USA); ethyl acetate and methanol (Sigma-Aldrich, Steinheim, Germany) were HPLC grade. All other reagents were commercially available at the local market and were of analytical grade.

2.2. Sample collection

The strawberries (Camarosa and Victoria) were harvested in mid-summer in the eastern part of Georgia (GPS coordinates: Latitude: 41°57'59.99" N, Longitude: 44° 05' 60.00" E). After harvesting, representative samples of the fruits were treated with combined solution (0.005% MJ, 0.15% SA, 1% AA) at 20±1 °C with an exposure time of 2.0 min. The treated

samples were stored in a refrigerator at 0 ± 0.5 °C and $95\pm 0.5\%$ RH. Quality parameters such as vitamin C content, TPC and anthocyanin content, as well as the antioxidant potential were monitored at the start of sampling and after 4,7,10 and 13 days.

2.3. Sampling procedure

The samples were prepared for the ascorbic acid determination by HPLC (Varian-Prostar-500, USA, detector-UV varian Prostar, Australia, column- 250 mm × 4.6 mm, dp = 5 µm (Symmetry, Waters, Ireland) [25] as follows: briefly, the sample (10 g) was extracted in 10 mL water adjusted to pH 1.5 with 10 mL phosphoric acid-water (2%, v/v). The extracts were filtered through 45 µm filter paper (Whatman, UK) and 1.5 mL buffer (0.01 M KH₂PO₄, pH 8.0) then added to 1.5 mL of the sample extract. 1 mL aliquots (vitamin C) of each of the preferred mixtures were then loaded on to C 18 cartridges (Agilent, Bond Elut, USA) and 3 mL aliquots of water adjusted to pH 1.5 with 2 mL phosphoric acid-water (2%, v/v) passed through them.

The samples used for the antioxidant analysis were prepared according to Rodriguez-Saona and Wrolstad (2001) [26]. About 40 g of strawberries was cryogenically milled in liquid nitrogen. Chilled test tubes were filled with milled fruit powder and weighed (5 g), and the powder then extracted with acetone (200 mL). The acetone was removed under vacuum in a rotary evaporator at < 30 °C, and 250 mL of methanol (70%) then added to the powder. The total methanol extract was examined for antioxidant activity.

Samples for anthocyanin analyses by High performance liquid chromatography, HPLC (Varian – Prostar - 500, USA, detector - UV varian Prostar, Australia, column – S 250 x 4.6, Agilent, Microsorb – 100 - 5, The Netherlands) were prepared according to Prior et al. (2012) [27]. Berries (40 g) were homogenized in methanol/water/formic acid in a ratio of 60: 37: 3 (v/v/v), kept overnight (14 h) at 3 – 5°C and later filtered by filter 45 µm (Whatman, UK) through a Buchner funnel under vacuum. The filtrates were centrifuged (4000 X g, 15min, 21°C) The supernatant was concentrated under vacuum in a rotary evaporator at < 30°C to total evaporation of the methanol. An aliquot (2.0 mL) of the aqueous phase was carefully deposited onto a C - 18 cartridge (Agilent, Bond Elut, USA). sugars and more polar substances were removed by passing 2.0 mL of ultrapure water through the cartridge. polyphenols were removed by passing 2.0 mL of ethyl acetate and finally anthocyanin pigments were eluted with 10 mL of methanol. 10 mL deionized (DI) water was added to the methanol extract and then the methanol was removed under vacuum in a rotary evaporator at < 30°C.

2.4. Determination of pH

pH value of the berry fruits was measured using a pH-meter (EHS-320, China) at 20°C [28].

2.5. Determination of vitamin C

Vitamin C was determined by the HPLC method [25]. The columns used were 250 mm × 4.6 mm, dp = 5 µm (Symmetry, Waters, Ireland) and the mobile phase was water adjusted to pH 3 with phosphoric acid. The UV detector (Varian pro Star, Australia) was set at 215 nm and quantification was based on the peak area measurement. For HPLC (Varian-Prostar-500, USA), 20 µL of sample were injected.

2.6. Determination of total Anthocyanins

The anthocyanins were quantified by the pH differential method [29]. Samples were diluted 1:150 in pH 1.0 and pH 4.5 buffers, and the absorbance measured at 520 nm and 700 nm in a UV -Visible spectrophotometer (A & E Lab Co LTD, UK), based on a

cyanidin 3-glucoside molar extinction coefficient of $26,900 \Delta\text{Emol}^{-1}$ and a molecular weight of 449.2 gmol^{-1} . The resulting values were expressed in terms of mg of anthocyanin per 100 g of fresh fruit.

2.7. Determination TPC

TPC was performed by Bond et al. (2003) [30]. As aliquot of 1.0 mL of diluted sample extract was vortexed with 10 mL DI water and 1.0 mL Folin-Ciocalteu reagent, and a 1.0 mL deionized water was used as control. After equilibration at room temperature for 8 min, the solutions were mixed with 4 mL of 7.5% (w/v) Na_2CO_3 . The samples and standards (Gallic acid dilute working standard solutions: $10\text{--}50 \mu\text{g mL}^{-1}$) were equilibrated at room temperature for 60 minutes. The absorbance of the samples and standards were measured spectrophotometrically (UV/Vis spectrophotometer, A&E Lab Co LTD, UK) at 765 nm, with a 10 mm path length cell. TPC was calculated as mg of gallic acid equivalents per 100 g fresh weight of sample.

2.8. Determination of individual anthocyanins by HPLC

Determination of Anthocyanins by HPLC Analyses was performed by a Varian – Prostar - 500 series liquid chromatograph. Separation was achieved on a C18, 150 mm x 4.6 mm column. Solvents used were: (A) Aqueous Trifluoroacetic acid (TFA) 0.1%, and (B) Methanol 100%, establishing the following gradient: isocratic 6% B for 5 min, 30% B over 10 min, isocratic 50% B for 15 min, 60% B over 5 min, and 6% B over 10 min, using a flow rate of 0.4 mL min^{-1} , using 518 nm wavelength, and a mass spectrometer (MS, Varian-prostar-500, USA) connected to the HPLC system. The Mass Spectrometer (MS) was equipped with an Electro Spray Ionization (ESI) source and an ion trap mass analyzer. Spectra were recorded in positive ion mode 3500 volts. Quantification of anthocyanins content was carried out according to chromatographic peaks at 518 nm wavelength.

2.9. FRAP assay

The Ferric Reducing Ability of Plasma (FRAP) assay was carried out as previously described by Benzie and Strain (1996) [31]. The experiment was carried out at 37°C and pH 3.6 with a blank sample in parallel. In the FRAP assay, the reductants (“antioxidants”) in the sample reduce the Fe (III)/tripyridyltriazine complex to the blue ferrous form, with an increase in absorbance at 593 nm. The final results were expressed as micromole AA equivalents per 100 gram ($\text{mmol AA}100\text{g}^{-1}$).

2.10. Texture Profile Analysis (TPA)

The texture analyses of the strawberries were carried out using a Texture Analyser (LLOYD, TA1, AMETEK Inc, USA). Cylindrical probe with 10 mm diameter was applied. Extension speed of the probe was 100 mmmin^{-1} . Work done by probe, which caused the sample to rupture, was calculated.

2.11. Statistical Analysis

The data represents the mean of three replicates \pm standard deviation (SD). Data were subjected to the *t* - test. All calculations were performed with Microsoft Excel (Version 4, statistical functions, Microsoft Corp., Redmond, WA, USA).

Results and discussion

3.1. pH

During storage period, pH value of treated as well as untreated fruits did not change statistically significantly and was between 3.60–3.76 for Victoria (Table 1) and between 3.75–3.99 for Camarosa (Table 2). This fact indicates that there was no hydrolyses of proteins and no change in organic acids concentration during storage period, i.e. conditions for cold storage was chosen properly.

Table 1

Proximate chemical composition of Victoria

Storage period		pH	Vitamin C mg100g ⁻¹	Total Anthocyanins mg100g ⁻¹	TPC mg100g ⁻¹	FRAP mg equivalents of vitamin C x 100g ⁻¹
Initial		3.60 ±0.18 ^a	45.60 ±2.28 ^a	21.35 ±1.06 ^a	129.86 ±6.49 ^a	206.46 ±10.32 ^a
After 4 days	C	3.69 ±0.18 ^a	56.40 ±2.82 ^b	17.09 ±0.85 ^b	134.23 ±6.71 ^a	185.70 ±9.28 ^b
	TS	3.79 ±0.19 ^a	61.20 ±3.06 ^b	20.21 ±1.01 ^a	140.85 ±7.04 ^a	202.12 ±10.10 ^a
After 7 days	C	3.68 ±0.18 ^a	52.80 ±2.64 ^b	15.79 ±0.78 ^b	130.92 ±5.23 ^a	136.08 ±6.80 ^c
	TS	3.80 ±0.19 ^a	55.20 ±2.76 ^b	19.50 ±0.97 ^c	137.56 ±6.87 ^a	177.25 ±8.86 ^b
After 10 days	C	3.77 ±0.17 ^a	41.00 ±2.05 ^c	13.95 ±0.69 ^d	126.57 ±6.32 ^a	130.38 ±6.51 ^c
	TS	3.82 ±0.20 ^a	49.25± ±2.46 ^d	18.91 ±0.94 ^c	141.95 ±7.10 ^a	169.14 ±8.45 ^b
After 13 days	C	3.76 ±0.17 ^a	22.55 ±1.12 ^e	13.35 ±0.66 ^d	111.15 ±5.55 ^b	120.02 ±6.00 ^d
	TS	3.95 ±0.20 ^b	38.95 ±1.94 ^f	15.49 ±0.77 ^b	138.00 ±6.90 ^a	157.61 ±7.88 ^e

*C-control; **TS-treated samples

*-Values within a column with different letters are significantly different by ANOVA with Tukey's HSD tests at p < 0.05.

3.2. Content of vitamin C

Vitamin C content in the fruits of Victoria increased after treatment from 45.60±2.28 to 56.40±2.82 mg100g⁻¹ in control samples and up to 61.20±3.06 mg100g⁻¹ in treated samples, and stayed on this level until 7-th day. Increasing of vitamin C content was caused, probably, because of the prolonged ripening process in fruits during first storage days [25]. After 7-th day content of vitamin C declined due to destruction of vitamins caused by oxidation process [32–36]. On the 13-th day, it was 22.55 ±1.12 and 38.95±1.94 mg100g⁻¹ in control and treated samples respectively. Thus, treatment with MJ, SA and AA positively influenced on the level of content of vitamin C in Victoria strawberries fruits during storage.

As to the fruits of Camarosa, because of oxidation process again, vitamin C content decreased monotonically in the control and treated samples as well, and at the end of experiment it was about half of the initial level. There was no statistically significant difference between content of vitamin C in the control and treated samples (Table 2). So, in case of Camarosa fruits, no effect of treatment with MJ, SA and AA on the content of vitamin C was found.

Table 2

Proximate chemical composition of Camarosa

Storage period		pH	Vitamin C mg100g ⁻¹	Total Anthocyanins mg100g ⁻¹	TPC mg100g ⁻¹	FRAP mg equivalents vitamin C x 100g ⁻¹
Initial		3.75 ±0.15 ^a	56.40 ±2.82 ^a	46.93 ±2.34 ^a	181.51 ±9.07 ^a	370.23 ±18.51 ^a
After 4 days	C	3.78 ±0.15 ^a	58.80 ±2.94 ^a	35.03 ±1.75 ^b	188.10 ±9.40 ^a	352.30 ±17.61 ^a
	TS	3.82 ±0.19 ^a	62.40 ±3.12 ^a	48.43 ±2.42 ^a	197.80 ±9.89 ^a	368.45 ±18.42 ^a
After 7 days	C	3.87 ±0.18 ^a	43.20 ±2.16 ^b	30.15 ±1.50 ^c	162.83 ±8.14 ^b	281.60 ±14.08 ^b
	TS	3.80 ±0.18 ^a	45.60 ±2.28 ^b	42.20 ±2.11 ^a	184.81 ±9.24 ^a	319.99 ±15.99 ^c
After 10 days	C	3.90 ±0.19 ^a	28.70 ±1.43 ^c	26.28 ±1.31 ^d	160.32 ±8.01 ^b	216.30 ±10.81 ^d
	TS	3.84 ±0.19 ^a	30.75 ±1.53 ^c	38.17 ±1.90 ^b	180.11 ±9.00 ^a	277.98 ±13.89 ^b
After 13 days	C	3.99 ±0.20 ^a	23.40 ±1.17 ^d	20.41 ±1.02 ^e	131.00 ±6.55 ^c	201.14 ±10.05 ^d
	TS	3.83 ±0.18 ^a	25.42 ±2.27 ^d	34.59 ±1.72 ^b	150.02 ±7.50 ^d	248.25 ±12.41 ^e

*C-control; **TS-treated samples

*-Values within a column with different letters are significantly different by ANOVA with Tukey's HSD tests at p < 0.05.

3.3. Content of total anthocyanins

Total anthocyanins in the control samples of Victoria gradually decreased from 21.35±1.06 to 13.35±0.66 mg100g⁻¹ on the 13-th day of storage. The reason for reduction of anthocyanins quantity may be their oxidation process [37]. As to the treated samples, anthocyanins content reduced to 15.49±0.77mg100g⁻¹. Difference between control and treated samples at the end of experiment was statistically significant but practically insignificant (Table 1).

In the samples of Camarosa total anthocyanins reduced from 46.93±2.34 to 20.41 ±1.02 and to 34.59±1.72 mg per 100 g fruits in control and treated samples respectively. Difference between control and treated samples at the end of experiment was statistically and practically significant as well (Table 2). Thus, in case of Camarosa, application of combined solution of methyl jasmonate, salicylic acid and ascorbic acid positively influenced on storability of strawberry fruits.

3.4. TPC

Total phenolic compounds in the control samples of Victoria initially was equal to $129.86 \pm 6.49 \text{ mg}100\text{g}^{-1}$ and at the end of experiment it reduced to 111.15 ± 5.55 , that is by 17%. Degradation of phenolic compounds was. Probably, caused by their oxidation [38.39]. Whereas, in the treated sample TPC was unchanged (Table 1), assumingly due to the treatment effect.

TPC in Camarosa initially was by 40% more than in Victoria, i.e. $181.51 \pm 9.07 \text{ mg}100\text{g}^{-1}$. After 13 days of storage, TPC reduced to 131.00 ± 6.55 and to $150.02 \pm 7.50 \text{ mg}100\text{g}^{-1}$ in the control and treated samples respectively (Table 2). Effect of treatment was statistically and practically significant. From these data, we can conclude, that combined solution of MJ, SA and AA effectively inhibited oxidation process of phenolic compounds in the fruits of strawberry of Victoria and Camarosa varieties.

3.5. FRAP assay

It is well known that antioxidant activity of fruits is proportional to the phenolic compounds content [40.41]. Therefore, it was not surprising that antioxidant activity monotonically decreased in the control samples of Victoria from 206.46 ± 10.32 at the first day to $120.02 \pm 6.00 \text{ mg}$ equivalents of vitamin-C per 100g fruits at the end of the experiment. Change in antioxidant activity of the treated samples of Victoria was less significant: from 206.46 ± 10.32 to 157.61 ± 7.88 units, that is by 17.9% less than in the case of control samples.

Antioxidant activity of fruits of Camarosa initially was by 80% more than that of Victoria fruits. During storage period, antioxidant activity of the fruits of Camarosa decreased gradually. After 13 days of storage, it was equal to 201.14 ± 10.05 and 248.25 ± 12.41 units for untreated and treated samples respectively (Table 2). Thus, the effect of treatment was statistically and practically significant, i.e. 23.3%.

3.6. Individual anthocyanins

Main anthocyanin in the fruits of both varieties was Pelargonidin-3-O-glucoside. This is a common case for strawberry fruits [42]. Its initial content in the fruits was 68.45 ± 3.42 and $65.28 \pm 3.26 \%$ of total anthocyanins for Victoria and Camarosa varieties respectively. Though total anthocyanins content gradually decreased during storage period, percentage of this anthocyanin did not change during storage days (Table 3). This indicates on the fact, that Pelargonidin-3-O-glucoside remained the main anthocyanin during whole period of storage. In Victoria variety Pelargonidin-3-acetyl-glucoside was the second anthocyanin by quantity – its percentage in the treated and untreated samples was about 10% and did not changed during storage. Percentage of this anthocyanin in the Camarosa variety varied non-monotonically during storage time. Non-monotonical changes of percentage of individual anthocyanins, assumingly, was a result of the fact that quantity of various anthocyanins were changing differently during storage period. In Camarosa Cyanidin-3-O-glucoside was the second anthocyanin by quantity, its percentage changed during storage period from 10.25 ± 0.51 to 9.41 ± 0.47 and $8.10 \pm 0.40\%$ for untreated and treated fruit samples respectively. Pelargonidin-3-O- rutinoside was one more anthocyanins detected in both varieties of strawberry. Its initial percentage was equal to 6.14 ± 0.30 and $8.23 \pm 0.41\%$ in Victoria and Camarosa varieties respectively. Cyanidin-3-O-rutinoside was presented in the smallest quantity in both varieties. Its percentage was less than 1% and did not change practically during storage time.

Table 3

Individual Anthocyanins in Strawberry cultivars (%)

Cultivars	Storage period	1	2	3	4	5		
Victoria	Initial	5.44 ±0.27 ^a	0.17 ±0.008 ^a	68.45 ±3.42 ^a	6.14 ±0.30 ^a	10.03 ±0.50 ^a		
	After 4 days	C	5.39 ±0.26 ^a	0.21 ±0.01 ^b	69.04 ±3.45 ^a	7.65 ±0.38 ^b	9.83 ±0.49 ^a	
		TS	6.30 ±0.31 ^b	0.19 ±0.009 ^c	69.19 ±3.46 ^a	6.45 ±0.32 ^a	9.13 ±0.45 ^a	
	After 7 days	C	7.71 ±0.38 ^c	0.23 ±0.01 ^d	65.95 ±3.29 ^a	7.44 ±0.37 ^b	10.33 ±0.51 ^a	
		TS	6.76 ±0.33 ^b	0.22 ±0.01 ^{bd}	66.87 ±3.34 ^a	6.59 ±0.32 ^a	10.06 ±0.50 ^a	
	After 10 days	C	5.23 ±0.26 ^a	0.20 ±0.02 ^{bd}	69.45 ±3.47 ^a	6.12 ±0.30 ^a	8.09 ±0.40 ^b	
		TS	6.19 ±0.38 ^a	0.24 ±0.01 ^d	68.01 ±3.40 ^a	7.33 ±0.36 ^b	9.38 ±0.47 ^a	
	After 13 days	C	8.27 ±0.41 ^c	0.23 ±0.01 ^{bd}	66.29 ±3.31 ^a	6.02 ±0.30 ^b	8.22 ±0.41 ^b	
		TS	8.69 ±0.43 ^c	0.35 ±0.02 ^e	64.84 ±3.24 ^a	5.47 ±0.27 ^c	9.10 ±0.45 ^a	
	Camarosa	Initial	9.28 ±0.46 ^a	0.48 ±0.02 ^a	65.28 ±3.26 ^a	8.23 ±0.41 ^a	7.01 ±0.35 ^a	
		After 4 days	C	10.25 ±0.51 ^a	0.63 ±0.03 ^b	65.40 ±3.27 ^a	11.71 ±0.58 ^b	3.13 ±0.15 ^b
			TS	7.81 ±0.39 ^b	0.46 ±0.02 ^a	68.68 ±3.43 ^a	8.72 ±0.43 ^a	4.12 ±0.20 ^c
		After 7 days	C	9.29 ±0.46 ^a	0.70 ±0.03 ^c	65.50 ±3.27 ^a	13.93 ±0.69 ^c	1.57 ±0.07 ^d
			TS	10.58 ±0.52 ^a	0.59 ±0.03 ^b	64.00 ±3.20 ^a	10.67 ±0.53 ^b	4.62 ±0.23 ^c
After 10 days		C	11.41 ±0.57 ^a	0.65 ±0.03 ^b	65.81 ±3.29 ^a	10.08 ±0.50 ^b	2.23 ±0.11 ^f	
		TS	9.12 ±0.45 ^a	0.31 ±0.01 ^d	62.73 ±3.13 ^a	4.11 ±0.20 ^d	12.26 ±0.61 ^g	
After 13 days		C	9.41 ±0.47 ^a	0.62 ±0.03 ^b	67.81 ±3.39 ^a	10.16 ±0.50 ^b	2.02 ±0.10 ^f	
		TS	8.10 ±0.40 ^b	0.32 ±0.01 ^d	63.73 ±3.18 ^a	4.00 ±0.20 ^d	11.30 ±0.56 ^g	

*C-control; **TS-Treated samples

1.Cyanidin-3-O-glucoside

2.Cyanidin-3-O-rutinoside

3.Pelargonidin-3-O-glucoside

4.Pelargonidin-3-O-rutinoside

5.Pelargonidin-3-acetyl-glucoside

* Values within a column with different letters are significantly different by ANOVA with Tukey's HSD tests at p <0.05

3.7. Texture analysis

The curve showing load resulting from deformation of fruit was linear for all samples (Fig.1). At the start of experiment for control samples of Victoria fruits, work required for rupture of fruits was equal to 20.6 ± 4.7 Nmm, and at the end of the experiment, it was equal to 10.8 ± 4.8 Nmm. For the treated samples of Victoria this parameter changed from 25.1 ± 9.8 to 17.8 ± 4.5 Nmm. Camarosa fruits were more resistant against load force. Work to rupture untreated samples of Camarosa was equal 46.5 ± 13.2 Nmm at the start of experiment and reduced to 30.4 ± 5.5 Nmm after 13 days of storage. As to the treated samples of Camarosa, this parameter was 43.2 ± 6.3 Nmm on the first day of experiment, and 32.6 ± 5.5 Nmm on the 13-th day of storage. Thus, treatment with combined solution resulted in improvement of texture of fruits during storage process.

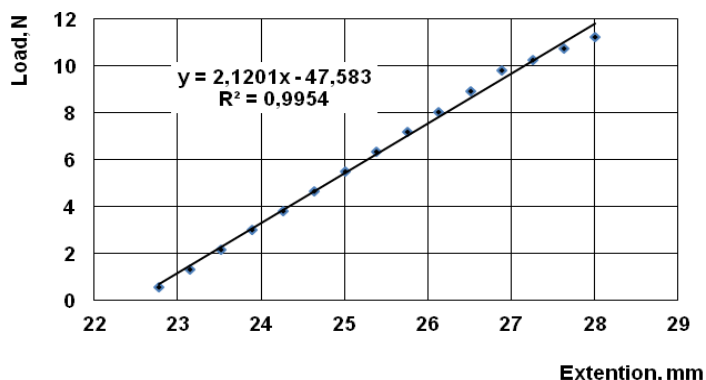


Figure 1. Load dependence on extension in camarosa fruits, control samples, first day

Conclusions

Treatment of fruits of strawberry with combined solutions of methyl jasmonate, salicylic acid and ascorbic acid positively influenced on storability of the fruits. Maintenance of anthocyanins and total phenolics as well as antioxidant potential during storage period was statistically significantly increased. Treatment with combined solution resulted in improvement of texture of fruits during storage process.

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Formation of the functional and technological properties of the beef minced meat by using the food additive on the nanopowder basis of double oxide of two- and trivalent iron

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Abstract

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Introduction. It is investigated the influence of the food additive on the nanopowder basis of double oxide of two- and trivalent iron for the quality and the technological properties of beef minced meat.

Materials and methods. The beef minced meat in which the nanopowder of double oxide of two- and trivalent iron was added in the amount of 0,05–0,15 %. The water – holding capacity and fat-retaining capacity was determined by using a butyrometer and a refractometer; stability of forage emulsions by centrifugation method; the degree of penetration and the marginal shear stress on a tapered plastomer: the stickiness – by the size of the effort of the separating of two surfaces connected by minced meat.

Results and discussion. Due to the large specific volume, protein affinity, bacteriostaticity, high chemical potential and thermal stability of the nanopowder of double oxide of two – and trivalent iron has sorption, complexing, emulsifying, water-holding and fat-retaining capacities. This contributes to the formation of the new functional and technological indicators of minced meat systems and improve the consumer characteristics of the finished products obtained from them.

The introduction of a food additive which is based on a nanopowder of double oxide of two- and trivalent iron in the beef minced meat in an amount of 0,05–0,15% to the meat mass contributes to the improvement of sensory (by 1,0–1,2 points on a 9-point scale) and the functional and technological indicators in comparison with the control: the water-holding capacity increases by 1,1–2,0%; the fat-retaining – by 1,2–2,6 %; the emulsifying capacity – by 1,3–2,0%; stability or stability of minced emulsions – by 1,4–2,1%; it also helps to reduce the level of total microbial contamination from $6,2 \times 10^5$ CFU/g in the control to $(5,1–5,8) \times 10^5$ CFU/g in samples enriched with Fe_3O_4 , that is, by 6,5–19,6%. The losses during the heat treatment of the experimental samples of chilled minced meat with the addition of 0,05–0,15% Fe_3O_4 are reduced by 14,4–18,4%.

The rational amount of a food additive on the basis of nanopowder of double oxide of two- and trivalent iron – 0,1% to the mass of meat raw materials is shown.

Conclusion. The food additive on the basis of nanopowder of double oxide of two- and trivalent iron improves the quality and the technological characteristics of the minced meat systems.

Introduction

At present time the increase in the meat quality with the low moisture in particular with PSE i DFD problems dictates the need to improve the existing technologies of meat products which permit the practical and effectively use of the meat formula with the indicated disadvantages. Therefore, the meat industry uses a variety of food additives-improvers: biologically active additives (BAA), enriched with essential micro-elements and probiotic (BAA) [1, 2]; protein formulation [3, 4]; water-retaining agents E450, E452 [3, 5]; acidity regulators: E451, acetic acid, lactic acid, E262 [3, 6]; spices, spice extracts, dextrose, thickeners E412, E410, E415 [5, 6]; amplifiers of taste and aroma E621 [6]; antioxidants – citric, tartaric and ascorbic acid, E316 [6, 7]; natural food colors, in particular, red rice [6]; flavors, in particular, IN [5, 7]; colorants, in particular, NaNO₃ [7].

One of the most common additives is glutamic acid E620 and its salts (E621, E622, etc.) without which almost any enterprise in the meat processing industry can't do today. These substances are able to enhance the products taste made from meat especially when using the low-grade stock causing a "sense of satisfaction". This property is called the "glutamine effect" [7]. However, food additives of this group do not bear any technological load which is why they are not necessary either [7].

Another group of food additives that are widely used in the meat industry there are the additives to improve the functional and technological indicators of the meat products, in particular, the increase in the water binding capacity (WBC) of the meat and meat products (sodium and potassium alginates [6, 8]; agar, carrageenan [8, 9]; gums: carob, guar, xanthan, konduk [6, 8, 10, 11]; insoluble dietary fibers of the different origin: wheat, soy, oat, pea, apple, citrus [12–14]; citrates [7, 15], food phosphates: pyro, tri- and polyphosphates [7, 8], cellulose, methylcellulose, to arboximethylcellulose [6–8, 13, 14]. However, they impair the quality and reduce the microbiological safety (as a result of high moisture content) and the economic performance of the product (due to the yield increasing and reducing of the finished products cost). Exceeding the recommended amount of phosphates [7, 8] and citrates [7, 13] leads to a loss of the products aroma taste and a pearl luster appears on the cut. The disadvantage of the insoluble dietary fibers [7, 13–14] is the instability of both high and low temperatures in the acidic media and the salts presence. The lack of insoluble dietary fiber [12–14] – lack of antioxidant and antimicrobial action. The need for accurate the alginates dosing [6, 8] makes it difficult to use them in the meat industry.

To improve the emulsifying capacity it is used the food emulsifiers based on fatty acids:fatty acids salts, mono- and diglycerides of fatty acids cetylated fatty acid [6, 7, 17]. However, they do not have an antioxidant effect.

In the meat processing plants for the improving of the nutrition value and the water-retention capacities it is used the various functional ingredients derived from the industrial by-products (skin, hooves, feathers, offal, etc.). They are used in the form of enriching powdered protein supplements [6, 19].

However these additives are characterized by a narrow focus and do not have a complex effect [19]. In the meat industry for improving of the nutrition value and quality of finished products it is used the natural phytosolids and probiotics [2, 20]. Their disadvantage is the functional properties loss during heat treatment. Nowadays to improve the quality and shelf life of the meat products the dietary supplements with antioxidant and antimicrobial effects of natural origin are used: essential oils, oils and fats [21, 22]. The disadvantages of these additives include the low water-retention capacity and the insufficient yield of finished products [21, 22].

Recently, silver, titanium dioxide and silicon dioxide nanopowders have been used as the polyfunctional food additives [23]. However the use of these additives in food products is very limited, since their functional, technological, microbiological, and physical-chemical parameters have not been studied sufficiently [23]

Thus, the well-known food additives-improvers, as a rule, separately allow to improve the certain functional and technological characteristics, the product quality; slow down the processes of oxidative, microbial damage; lengthen storage time. However, they do not have a complex action.

Therefore, it is relevant in the meat-processing industry to search for and research the food polyplastic additives of the complex action.

For the formation of the necessary functional and technological properties of the meat products can be offered a dietary supplement based on iron oxides “Magnetofood” [Patent UA No. 126502 Food additive “Magnetofood”, 2018, Bul. No. 12, 4 p., Ukrainian Engineering Pedagogical Academy, Kharkov, Ukraine], which is a scientific development of the authors of this research paper. “Magnetofood” is a highly dispersed nanopowder with a particle size of 70 – 80 nm and with a large specific surface and chemical potential [24 – 28]. According to the chemical formulation “Magnetofood” is a double iron oxide ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$ або Fe_3O_4) which was obtained by the using the improved technology that allows to obtain nanoparticles of a given size; adjustment the physical-chemical and functional-technological properties; reduce the process complexity and the cost of the final product [24, 29 – 31]. Due to Fe (II), “Magnetofood” shows the reducing properties and can be used as an antioxidant additive which prevents the fats oxidation and fat-containing products and thereby improves their quality and the period of use [32, 33]. Considered the biological compatibility of the supplement “Magnetofood” with the living organisms and its positive effect on the human body [24, 34] it is possible to use the food additive based on Fe_3O_4 nanopowder (“Magnetofood”) as an additional source of the easily digestible iron [24, 35].

Nanoobjects which include a nanopowder based on Fe_3O_4 iron oxides (“Magnetofood”) have a huge potential and carry a lot of the important fundamental discoveries, the new functional-technological properties and promising technological applications [36, 37].

The nanoparticles interaction of a food additive based on Fe_3O_4 nanopowder (“Magnetofood”) with biopolymers (proteins, proteins, carbohydrates, lipids) it is a complex of the complex chemical reactions. The process of nucleation is nucleation of a new stable phase with an initial metastable phase passes through. The supramolecular organization of “Magnetofood” nanoparticles and the organic matrix structure play an important role. The result is the formation of spatial nanostructures that significantly affect on the functional and technological properties of raw materials and semi-finished products. In food systems such additives in particular, a food additive, based on Fe_3O_4 nanopowder (“Magnetofood”) can show restorative, antioxidant, bacteriostatic, sorption, complexing, emulsifying, water-binding, water-retaining, greasy properties [24, 38–42].

The researchers of VM Pasechny, TA Shugurova, NN Tolkunova and others have devoted their research to the modern directions of the technologies perfection for the meat split-off semifinished products. In numerous scientific publications the innovative approach prospects to the development or the technology improvement of the meat-split semifinished products are considered both in the aspect of the formation of the formulation with the use of additive- improvers and the technological process improvement [43–47].

Hence, the advanced way of the issue solution of the improving technological, sensory qualities and ensuring their stability and safety, extending the meat products shelf life, in particular, split semis can be used the new food ingredients which designed to perform, as a rule, the several functions at the same time: the structure formers, stabilizers, emulsifiers,

antioxidants; to possess bacteriostatic, water-retention and fat-containing capacities [45-47].

Therefore, the research related to the technology improvement of the high-quality meat products with a long shelf life with the food additives of complex action is relevant and well-timed.

Also the unknown effect of the food additive based on Fe_3O_4 nanopowder ("Magnetofood") on the sensory characteristics, the structural and mechanical and functional-technological properties of the meat-split semi-finished products, in particular, the beef mincemeat in the beef steaks technology.

As this research is the integral part of the authors' scientific and practical work for the beef steaks technology improving of a food additive using based on Fe_3O_4 nanopowder ("Magnetofood"), the aim of this work is to research the functional and technological properties of the beef minces by using of the food additives of Fe_3O_4 nanopowder ("Magnetofood") and determine the rational mass fraction of its addition.

To achieve the aim the following tasks were set:

- to investigate the effect of "Magnetofood" food additive on the heat treatment losses and sensory characteristics of prototypes of chilled beef mince after storage for 24 hours at $5\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$;
- to investigate the influence of "Magnetofood" food additive on the functional and technological properties of prototypes of fresh made and chilled beef mince after storage for 24 hours at $5\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$;
- to investigate the influence of "Magnetofood" food additive on the microbiological indicators of the test samples of fresh made and chilled beef mince after storage for 24 hours at $5\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$;
- to investigate the influence of "Magnetofood" food additive on the structural and mechanical properties of the experimental samples of fresh made beef mince;
- to establish a rational mass fraction of "Magnetofood" food additive in the experimental samples of the beef mince.

Materials and methods

Materials

Object of research: the effect of the food additive based on Fe_3O_4 nanopowder ("Magnetofood") on the heat treatment losses; the functional and technological (emulsifying, water-binding, water-retention and fat-containing capacities, the stability of beef mince emulsion) and the structural-mechanical (ultimate shear stress, stickiness), and the properties; the sensory and microbiological (the level of total microbial contamination – NMAFAnM, the number of bacteria of the coliform bacterium group – BCBG, bacteria of the genus *Salmonella* and *L. Monocytogenes*) the indicators of beef minced meat.

Research subjects:

- sample 1 control is beef mince. For its preparation the meat was taken: prime beef or the first quality. After cleansing and degreasing, the beef was ground on a meat grinder with a diameter of the openings of the output grating of 3 – 4 mm. Then the sample was thoroughly mixed with salt and spices and held for 10 minutes;
- sample 2 is beef mince which was prepared as in sample 1. Only a mixture of the spices, salt and nutrient additive based on Fe_3O_4 nanopowders ("Magnetofood") was

added to the crushed beef (the amount of the additive was 0,05% relative to the meat raw mass). Then the sample was thoroughly mixed and held for 10 minutes;

- sample 3 is beef mince which was prepared like sample 1. Only a mixture of spices, salt and food additive based on Fe_3O_4 nanopowder (“Magnetofood”) was added to the crushed beef (the amount of additive was 0,10% relative to the meat raw mass). Then the sample was thoroughly mixed and kept for 10 minutes.
- sample 4 is beef mince which was prepared like sample 1. Only a mixture of spices, salt and food additive based on Fe_3O_4 nanopowder (“Magnetofood”) was added to the crushed beef (the amount of additive was 0,15% relative to the meat raw mass). Then the sample was thoroughly mixed and kept for 10 minutes.

All samples were stored in a vacuum package at a temperature of (5 ± 1) °C for 24 hours, the heat losses were investigated; their emulsifying, water-binding, water-retention and fat-containing capacities; emulsion stability; the rheological characteristics (shear stress, stickiness) are the microbiological (the level of total microbial contamination is NMAFAnM, the number of bacteria of the coliform bacterium group – BCBG, bacteria of the genus *Salmonella* and *L. Monocytogenes*) and the sensory indicators (appearance, sectional view, consistency, odor and taste).

Food additive based on iron oxides (“Magnetofood”) [Patent UA No. 126502 Food additive “Magnetofood”, 2018, Bul. No. 12, 4 p., Ukrainian Engineering Pedagogical Academy, Kharkov, Ukraine], which is a scientific development of the authors of this research paper. “Magnetofood” is a highly dispersed nanopowder of brown or black color with a particle size 78 nm. According to the chemical composition of “Magnetofood” is a double ferrous oxide ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$ or Fe_3O_4) obtained by the method of the chemical coprecipitation from aqueous solutions of salts of two- and trivalent ferrum in the alkaline medium.

Methods

In the researches the mince recipe for beef steak was chosen as the basic formula [48].

In the process of performing experimental work the research methods were used which are given in [40, 49, 51].

The heat treatment of the experimental samples of the minced meat was carried out by the frying method in the main way at a frying surface temperature of 150-160°C till the temperature of culinary readiness in the center of the product is reached (85 ± 1) °C.

Losses determination during the heat treatment and sensory parameters of the experimental samples of beef mince

In the final meat solid products it was researched the finished product yield (FPY) and heat treatment losses (HTL) which was determined as the difference in the case of the initial semi-finished product and the finished product in accordance with the methods [49, 51].

Sensory estimation of the minced meat quality and products made from them was carried out on a 9-point scale in accordance with [40, 49, 50]. To estimate of the minced meat quality from beef and made of meat split products according to sensory indicators, the study samples were taken from the different places of the stuffing mass depending on the volume and from 3 to 7. The appearance of minced meat semi-finished products was determined visually raw and fried. The quality of beef (grinding degree, equability mixing, texture) was determined visually. The smell and taste of minced meat and split meat semi-

finished products, as well as fried products made from them, were determined organoleptically at the cut. Moreover, the appearance and smell of the fried products was determined sensory in the hot condition (the product temperature is not lower than 65 °C) and the taste after cooling the product to a temperature of 25–30 °C.

The degree of grinding and equability mixing of the minced meat and also the correctness of split products heat treatment made from them were determined visually in the hot products (the product temperature is not lower than 65 °C), for which each product was cut into four parts (along and across through the middle).

Determination of functional and technological properties of the beef mince prototypes

The water-holding capacity (WHC) was determined by using a butyrometer according to the method [49]. The sample of minced meat portion weighing 4–5 g was thoroughly crushed. The glass rod was uniformly applied to the inner surface of the milk butyrometer which was punched with a stopper and placed narrowly into the water bath at a boiling temperature for 15 min. After that the moisture mass was determined according to the amount of division on the scale of the butyrometer. Water-holding capacity (WHC) of the minced meat (%) was determined by the formula (1):

$$\text{WHC} = W - \text{WHLC} \quad (1)$$

water-highlighting capacity (WHIC) of the minced meat (%) (2):

$$\text{WHIC} = a \cdot m \cdot n^{-1} \cdot 100, \quad (2)$$

W – is the total mass fraction of moisture in the weight, %;

a – is the price of dividing the butyrometer; $a = 0,01 \text{ cm}^{-1}$;

n – is the number of divisions on the zymometer scale;

m – is the sample weight, g

Fat-retaining capacity (FRC) was determined by using a butyrometer and refractometer according to the method [49]. The MPC was preliminarily calculated and the minced meat weight was found that remained in the oil with an accuracy of $\pm 0,0001 \text{ g}$. The sample was placed in a tube and dried to a post mass at 150 °C for 1,5 hours. After drying, the sample weighing $(2,0000 \pm 0,0002) \text{ g}$ is placed in a porcelain mortar, 2,5 g ($1,6 \text{ cm}^3$) of fine calcined sand and 6 g ($4,3 \text{ cm}^3$) α -monobromo-naphthalene are added. The contents of the mortar were carefully ground for 4 minutes and filtered through the folded paper filter.

The investigated solution (3–4 drops) was evenly applied to the lower prism of the refractometer with a glass rod. The prism was closed by fastening the screw. The beam of light was directed with the help of a mirror on the prism of the refractometer, setting the sight tube so that the borders of the intersecting fields (aliada) were clearly visible. Aliada moved until the boundary between the illuminated and the dark fields did not coincide with the intersection point of their limits, counting the index of refraction. At the same time the refractive index of α -monobromonaphthalene was determined. Fat-retaining capacity of forcemeat (FRC) (%) was determined by the formula (3):

$$\text{FRC} = g_1 \cdot g_2^{-1} \cdot 100, \quad (3)$$

where g_1 – is the fat mass fraction in the weight after the heat treatment, %;

g_2 – is the same one before the heat treatment, %.

The emulsifying capacity (EC) and the stability or the emulsion stability (ES) were determined according to the procedure [49, 50]. A portion of ground beef by the weighing

7 g is suspended in 100 cm³ of the water in a homogenizer at a frequency of 66,6 s⁻¹ for 60 s. 100 cm³ of the sunflower oil are added and the mixture is emulsified in a homogenizer at a speed of 1500 s⁻¹ for 5 minutes. Then the emulsion is poured into 4 calibrated centrifugal tubes with a volume of 50 cm³ and centrifuged at 500 s⁻¹ for 10 minutes. It is determined the volume of the emulsified oil. The emulsifying ability (EC) (%) was determined by the formula (4):

$$EC = V_1/V \cdot 100 \quad (4)$$

where V_1 – is the volume of the emulsified oil, cm³;

V – is the total volume of oil, cm³.

The emulsion stability (ES) was determined by the heating at a temperature of 80 °C for 30 minutes. and the cooling water for 15 minutes. Then emulsion was filled with 4 calibrated centrifuged tubes in a volume of 50 cm³ and centrifuged for 500 s⁻¹ for 5 minutes. It is determined the volume of the emulsified layer. The emulsion stability (ES) (%) was determined by the formula (5):

$$ES = V_1/V_2 \cdot 100 \quad (5)$$

where V_2 – is the total volume of the emulsion, cm³

R.M. Salavatulina determined the **WHC**, **FRC** and the stability of the stuffing emulsions (SE) in one weight [49, 51].

The minced meat samples by the weighing 180–200 g, were placed in the hermetically sealed cans № 3, weighed and subjected to the heat treatment with the modes corresponding to the production (cooking at temperatures of 78–80 °C for 1 hour, cooled in the running water to a temperature of 12–15 °C).

The cans were opened the broth and the fat released were transferred into pre-weighted cans. After removing the broth and fat, minced meat was blotted with filter paper and weighed. Buks with broth were placed in a drying cabinet and dried to constant weight at a temperature of 103–105 °C. The mass fraction of moisture released during the heat treatment of minced meat and the water-holding capacity of minced meat were determined. From the cups with the rest of the broth and fat, the fat was extracted in 10–15 cm³ of solvents, (a mixture of chloroform and ethanol in a 1: 2 ratio). The fat extraction was carried out for 3 to 4 minutes from three to four replicates. Having established the mass fraction of the fat remaining after the heat treatment of minced meat it was calculated the grease capacity. The stability of the stuffing emulsion (% by weight of meat) was determined by the formula (6).

$$SE = (m - m_{b1}/m) \cdot 100, \text{ or } SE = m_b/m \cdot 100, \quad (6)$$

where $m = m_{tk} - m_t$;

$m_{b1} = m - m_b$;

m – mass of minced meat, g;

m_{b1} – mass of broth with highlighted fats, g;

m_b – mass of the bunch of the minced meat after the heat treatment, g;

m_{tk} – mass of tight cans with fork stuffed, g;

m_t – the weight of cans, g

WHC of the minced meat (% to the weight of minced meat) was determined by the formula (7):

$$WHC = ((W - m_{b1} \cdot m_b) / m_{b2} \cdot m) \cdot 100, \quad (7)$$

where W – the mass fraction of moisture in the minced meat, %;

m_b – the mass in the investigated broth, g;

m_{b2} – the mass of the broth investigated with fat, g.

FRC of the minced meat (% to the weight of minced meat) was determined by the formula (8):

$$\text{FRC} = F_f - m_{61} \cdot m_{fb} / m_{62} \cdot m, \quad (8)$$

where F_f – the fat mass fraction in the minced meat, %;

m_{fb} – the fat body mass in the investigated broth, g.

Determination of microbiological parameters and structural and mechanical properties of test samples of beef minced meat

The list of the microbiological indicators used to control the quality of minced meat was established following the requirements: the number of mesophilic aerobic and facultative anaerobic microorganisms (NMAFAnM, KUO/g); the presence of bacteria in the group of coliform bacterium (BGCB (coliform), in 0,001 g); detection of the golden staphylococci, protein and other pathogenic microorganisms (pathogenic microorganisms including bacteria of the genus Salmonella, in 25 g) [40, 44, 45].

With the structural-mechanical (rheological) properties of the minced meat the degree of penetration (h) and ultimate shear stress (θ_0) on a conical plastomer were determined using a conical identifier [49].

The experimental sample of the beef minced cooking is made of the appropriate consistency and placed in the device cuvette. Align the surface of the experimental sample with the metal ruler so that the minced meat in the cuvette is level with its edges. A cuvette with a prototype set on the table of the instrument and raised up to the touch of the surface with the edge of the cone. Press the start button, turn on the stopwatch and holding the bar at a slight pace lower the cone. As the immersion cone like minced meat fixes the depth of immersion of the corrugated cone through the indicator every minute. Dipping ends in 3–5 minutes as at the end of this time the cone drops to a slight depth which can be practically neglected. The immersion drainage from 180 to 300 s corresponds to the largest period of relaxation of meaty minced meat from the beef used for research.

Fix the magnitude of the angle 2α at the vertex of the cone and the cone constant C (m/kg), the total mass of m_{tot} (kg) of the rod, the mass of the cone (m_{ind}) and the mass of the additional load (m_{ad}) by its presence. It is known that the depth of the immersion of a conical ident (h_{ind}) is equal to the degree of penetration (h) and is a function of the total mass, that is, according to the formula (9):

$$h = h_{ind} = f(m_{tot}), \quad (9)$$

where h_{ind} – depth of immersion of a conical ident, mm;

h – degree of penetration of the prototype, mm;

m_{tot} – total weight of the bar of the cone plastomer, kg

Hence, the estimated value of the mass of goods was determined by the formula (10):

$$m_{tot} = m_{ad} + m_{ind}, \quad (10)$$

where m_{tot} – is the total weight of the bar of the tapered plastomer, kg;

m_{ad} – is the mass of additional load, kg

m_{ind} – mass of cone identifier, kg.

For each sample, the boundary shear stress θ (Pa) was calculated for a fixed immersion duration (h) by the formula (11):

$$\theta = K \cdot m / h^2 = K \cdot m_{tot} - m_{ind} / h^2, \quad (11)$$

where m_{tot} – is the total weight of the bar of the tapered plastomer, kg;

m – the weight of the experimental sample, kg;

m_{ind} – the mass of conical identifier, kg;

C – the constants of the cone of the ident;
h – the depth of immersion of a conical ident, mm.

The arithmetic mean of the marginal shear stress (θ) for each of the variants (θ_i) of the experimental sample (i) was determined by the formula (12):

$$\theta = \sum \theta_i / i, \quad (12)$$

where θ – is the arithmetic mean value of the marginal strain of displacement, Pa;

θ_i – is the strain of the displacement of the experimental sample of minced beef, Pa
i – the number of samples of the beef minced samples.

The liposynthesis (ρ_o) was investigated on Sokolov-Bolshakov device which was based on the determination effort amount required to separate the two surfaces of the bound (bonded) minced meat that is being investigated. Adhesion or adhesion (Pa) was calculated as the specific force of the normal separation of the plate from the prototype minced meat from the beef by the formula (13):

$$\rho_o = F_o / S_o = 9,81 \cdot m / F_o \quad (13)$$

where F_o – is the separation force, N;

S_o – the geometric area of the plate, m^2 ;

m – the weight of the load, kg.

Results and discussion

Table 1 and Figure 1 show the of the heat treatment losses and sensory evaluation data of the cooled experimental samples of the beef minced meat.

Table 1

The losses results due to the heat treatment and the sensory parameters of the experimental samples of the cooled minced beef (on a 9 – point scale)

Name of the indicator	The experimental samples of the minced beef			
	Sample 1	Sample 2	Sample 3	Sample 4
The heat treatment losses %	20,6	18,0	17,5	17,4
Appearance	8,0±0,2	9,0±0,2	9,0±0,2	9,0±0,2
Appearance in the sections	8,0±0,2	9,0±0,2	9,0±0,2	8,0±0,2
Consistence	7,0±0,2	8,0±0,2	9,0±0,2	9,0±0,2
Scent and taste	8,0±0,2	9,0±0,2	9,0±0,2	9,0±0,2
Averaged scoring value	7,8±0,2	8,8±0,2	9,0±0,2	8,8±0,2

The analysis of the experimental data in the Table 1 shows that when introducing a food additive based on Fe_3O_4 nanopowders (“Magnetofood”) in the experimental samples of the cooled minced beef the losses amount in their heat treatment is reduced with the increase in Fe_3O_4 content by 14,4–18,4%.

The data given in Table 1 and Figure 1 indicate a positive effect of the adding Fe_3O_4 nanopowders to meat stuffing systems. The sensory parameters of the experimental samples of the cooled minced beef enriched with a food additive based on Fe_3O_4 nanopowder (“Magnetofood”) are improved. The average scoring value for the sensory parameters increases by 1,0–1,2 points in comparison with the control.

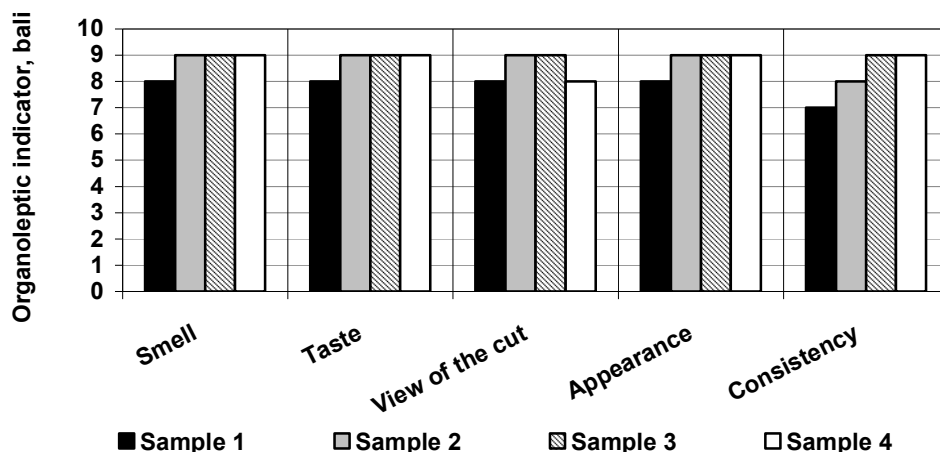


Figure 1. Sensory indicatory quality of the experimental samples of cooled minced beef

The introduction of a nutritional supplement based on Fe_3O_4 nanopowder (“Magnetofood”) and its ability to the electrostatic and coordination interaction with proteins of meat forages systems leads to the changes in the moisture content of the experimental samples and the water-retaining capacity of minced meat and consequently changes in the heat treatment losses whose the value decreases with increasing Fe_3O_4 content [29]. The optimum mass fraction of Fe_3O_4 additives which provides the best sensory characteristics of meat sausages and less heat treatment losses is 0,10 %.

The water-holding (WHC) and fat-retaining (FRC) capacity causes the product properties to store in it the prescribed amount of moisture and fat in the cooking process. Therefore, these characteristics are the main functional and technological properties of the meat forages systems. In the heat treatment process of the meat cut trunks and the physical and chemical changes of the ingredient composition occur. The part of moisture and fat are separated in the form of bouillon-fatty flushes which shows the result in the mass loss. As part of the finished product the moisture and fat retained and the amount determines the moisture and fat-retaining capacity of minced meat [28].

Table 2 presents the main functional and technological properties of the experimental samples of beef minced meat: WHC and FRC and the emulsifying capacity (EC), emulsion stability (ES) when adding the additive based on Fe_3O_4 nanopowder (“Magnetofood”) compared to control.

In the experimental samples of freshly prepared beef minced there is a gradual increase in WHC, FRC, EC, ES with an increase in Fe_3O_4 mass fraction in comparison with the control sample: WHC is increased by 1,1–2,0%; FRC by 1,2–2,6%; EC by 1,3–2,0%; ES by 1,4–2,1%.

The similar dynamics changes in these indices and in the experimental samples of cooled minced meat in 24 hours of their storage at $6\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$ only in all cases their value is lower by 1,3%–2,0% compared to freshly prepared beef minced meat. The best result is obtained with Fe_3O_4 mass fraction of 0,10%. Further increase of Fe_3O_4 to 0,15% practically does not affect the indicators change.

Table 2
Functional and technological properties of freshly prepared and the cooled beef minced meat after storage with the addition of a nutritional additive based on Fe₃O₄ nanopowder (“Magnetofood”) in comparison with the control sample

Name of the indicators		The experimental samples			
		Sample1	Sample2	Sample 3	Sample 4
WHC, %	freshly prepared beef minced meat	76,3±0,9	77,2±0,9	77,6±0,9	77,7±0,9
	in 24 hours of the storage at 6±1 °C	75,3±0,9	76,7±0,9	77,1±0,9	77,2±0,9
FRC,%	freshly prepared beef minced meat	72,1±0,7	73,3±0,8	73,8±0,9	73,9±0,8
	in 24 hours of the storage at 6±1 °C	71,6±0,7	72,7±0,8	72,9±0,9	73,0±0,8
EC,%	freshly prepared beef minced meat	78,2±0,9	79,2±0,9	79,5±0,9	79,8±0,9
	in 24 hours of the storage at 6±1 °C	77,2±0,9	77,9±0,9	78,3±0,9	78,4±0,9
ES,%	freshly prepared beef minced meat	80,2±0,8	81,3±0,8	81,6±0,9	81,7±0,8
	in 24 hours of the storage at 6±1 °C	79,2±0,8	79,9±0,8	80,2±0,9	80,3±0,8

The surface-active, sorption, complexing properties of the ionized nanoparticles of a food additive based on Fe₃O₄ nanopowder (“Magnetofood”), its catalytic activity, heat treatment stability, bio-affinity of the main component of “Magnetofood” – Fe₃O₄ nanoparticles with a lot of proteins determine the emulsifying, wetting, wet and fat-retaining capacity of “Magnetofood” [39]. Therefore, the introduction of the additive “Magnetofood” to meat minced meat increases the level of moisture and fat content and the formation of stable emulsions, in particular, with the lipid and protein components of meat sausage systems.

On the sanitary well-being of meat minced meat enriched with a food additive based on Fe₃O₄ nanopowder (“Magnetofood”) were judged by the microbiological parameters in accordance with [40, 44, 45]. The microbiological characteristics of freshly prepared (*) and cooled beef minced meat (**) were researched after storage at a temperature of – 5 °C ± 1 °C for 24 hours. The data obtained are presented in Table 3.

It can be seen from Table 3, the level of general microbial contamination of both freshly prepared minced meat and those stored for 24 hours at a temperature of – 5 °C ± 1 °C did not exceed the permissible levels and was: after the end of the technological process and cooling $5,0 \times 10^4$ CFU/g – in all prototypes; and after 24 hours of storage – $6,2 \times 10^5$ CFU/g in the control and $(5,1-5,8) \times 10^5$ CFU/g in the samples enriched with Fe₃O₄ that is, on 6,5–19,6% less than in the control sample. In this case in all experimental samples bacteria of the group of intestinal sticks (BGIS) in 0,001 g, bacteria of the genus Salmonella and L. Monocytogenes were not detected in 25 g.

Table 3
Microbiological characteristics of the fresh and cooled beef minced meat with the addition of a food additives on the basis of the Fe₃O₄ nanopowder (“Magnetofood”) compared to the control

The experimental samples	(NMAFAnM, CFU/g)	BGIS, in 0,001 g	Salmonella, in 25 g	L. Monocytogenes, in 25 g
*Sample 1	5,0×10 ⁴	missing in 0,001 g	missing in 25 g	missing in 25 g
**Sample 1	6,2×10 ⁵	missing in 0,001 g	missing in 25 g	missing in 25 g
* Sample 2	5,0×10 ⁴	missing in 0,001 g	missing in 25 g	missing in 25 g
** Sample 2	5,8×10 ⁵	missing in 0,001 g	missing in 25 g	missing in 25 g
* Sample 3	5,0×10 ⁴	missing in 0,001 g	missing in 25 g	missing in 25 g
** Sample 3	5,2×10 ⁵	missing in 0,001 g	missing in 25 g	missing in 25 g
* Sample 4	5,0×10 ⁴	missing in 0,001 g	missing in 25 g	missing in 25 g
** Sample 4	5,1×10 ⁵	missing in 0,001 g	missing in 25 g	missing in 25 g
Standard	1 × 10 ⁶	not allowed	not allowed	not allowed

Note. * – fresh beef minced meat

** – cooled beef minced meat

Reducing of the total microbial contamination in the cooled meat minced meat indicates the bacteriostatic effect on the food additive based on Fe₃O₄ nanopowder (“Magnetofood”). The obtained data also indicates that the meat minced from the beef enriched with “Magnetofood” when stored in a refrigerated state for 24 hours, complied with the requirements of the microbiological standards established for this type of product [40, 44, 45].

The most complete picture of some essential aspects of the quality of meat stuffings is the physical properties that depend on the biological and chemical composition (formulation) and the internal structure (product structure). Minor changes in these defining characteristics should cause the significant changes in the properties values that are registered by devices. At the same time the characteristics of the meat raw materials determine the main indicators of finished products. One of the groups of such indicators include structural – mechanical (rheological) properties.

Table 4 shows the results of determining the depth of immersion and (or the degree of penetration), h and the marginal displacement stress, θ^0 .

From the experimental data of Table 4 it follows that with the increase in the angle of the cone, the marginal shear stress (θ^0) decreases for all experimental samples of the minced meat. At the same time θ^0 in the experimental sample of 3 meat minced with a food additive based on Fe₃O₄ nanopowders (“Magnetofood”) in the optimum amount of 0,10 % by the meat weight is less than 26 % on average than in the control sample minced without Fe₃O₄. This indicates a softer and tender consistency of the beef minced with the addition of a nutritional supplement based on Fe₃O₄ nanopowders.

When forming a monolithic structure of the crushed meat the index of stickiness or adhesion (Ro) is the great importance [25, 28]. The research of stickiness for example, the sausage minced allows you to determine the optimal time of rubbing. Similarly in the state of the meat surface it is possible with a certain plausibility to assess its water-holding capacity. Stickiness is associated with other phenomena and products properties: adhesion, cohesion, viscosity and surface friction [48, 51].

Table 4
Structural – mechanical properties of the beef minced meat with the addition of the food additive based on Fe₃O₄ nanopowder (“Magnetofood”) compared with the control.

The angle of the cone α , deg.	Load F , H	Depth of immersion h , mm		Average depth diving h_{av} , mm		Tensile displacement of the experimental samples of the beef minced meat θ_0 , Pa “A”/ “B”					
		Sample 1 or “A”	Sample 3 or “B”	“A”	“B”	$C_{\alpha 1}$	$C_{\alpha 2}$	$C_{\alpha 3}$	$C_{\alpha 4}$	$C_{\alpha 5}$	
30°	1	0,25	4,65	4,25	4,70	4,20	12,5	12,0	11,5	11,8	12,2
	2	0,25	4,70	4,20			/9,5	/9,0	/8,5	/8,9	/8,4
	3	0,25	4,75	4,30							
60°	1	0,15	4,20	3,25	4,15	3,20	7,5	7,0	6,5	6,8	7,4
	2	0,15	4,15	3,20			/6,0	/5,8	/5,3	/5,7	/5,6
	3	0,15	4,25	3,15							
**	1	0,50	12,90	9,65	12,85	9,70	16,5	16,0	15,5	15,8	16,2
	2	0,50	12,85	9,70			/11,0	/10,5	/10,0	/10,4	/10,3
	3	0,50	12,80	9,75							

***Note.** ** – thin core; sample 1 or “A” is the control sample of the beef minced (without “Magnetofood”); sample 3 or “B” is the sample of the beef minced with the addition of a rational quantity of “Magnetofood” – 0,10%; C_{α} is the value of the constant of the cone for the different angles of the cone (30°/60°): ($C_{\alpha 1} = 1,110/0,415$ – P. A. Rebinder; $C_{\alpha 2} = 0,959/0,214$ – M. M. Agranat, M. F. Shirokov; $C_{\alpha 3} = 0,456/0,164$ – V.O. Aret, O.N. Pirogov, $C_{\alpha 4} = 0,663/0,213$ – A. V. Gorbatov, V. D. Kosoy.; $C_{\alpha 5} = 0,976/0,210$ – V. D. Karpichev, V.D. Kosoy.

The results of the research of stickiness content of the beef minced meat with the addition of a nutritional additive based on Fe₃O₄ nanopowders (“Magnetofood”) as compared to the control are given in Table 5 and Figure 3.

Table 5
The stickiness of the beef mince with the addition of a dietary additive based on Fe₃O₄ nanopowder (“Magnetofood”) compared with the control

The experimental samples of the beef mince	Contact pressure, $R_k \times 10^{-4}$, H/M ²	Stickiness, $R_0 \times 10^{-4}$, Pa
Sample 1-control	0,80	0,60
Sample 2	0,86	0,75
Sample 3	0,92	0,80
Sample 4	1,29	0,85

The analysis of data in Table 5 and Figure 2 shows that the use of beef minced meat on the basis of Fe₃O₄ nanopowder by helping to increase the stickiness content of meat minced meat at (0,15–0,25) × 10⁻⁴ Pa. Moreover with the increase in the mass fraction of the additive on the basis of Fe₃O₄ nanopowder (“Magnetofood”) the stickiness of the meat mints increases in 1,16–1,42 times compared with the control sample.

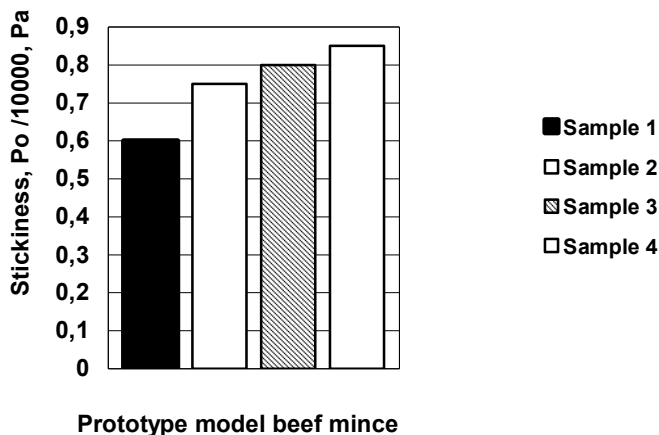


Figure 2. The influence of nutritional additive based on Fe_3O_4 nanopowder (“Magnetofood”) on the stickliness of the experimental samples of the beef minced meat

This is probably due to the intracellular enzymes activation as a result of the interaction of the ionogenic groups of their proteins with polarized Fe_3O_4 nanoparticles and the formation of the “biopolymer matrix of the enzyme – the nanoparticle of the magnetofoot (Fe_3O_4)” [38, 39].

The complex of the structural and mechanical indicators of the crushed raw material is the information that objectively characterizes the consistency features and is in the close correlation with the specific sensory perception of the latter in the process of disintegration and plasticization of the product in the oral cavity.

The results of research of the nutritional supplement influence on the basis of Fe_3O_4 nanopowder (“Magnetofood”) on the ultrasound WHC, FRC, EC, ES and on the stickliness of the beef minced meat indicate that the effective action of Fe_3O_4 additive nanoparticles is based on the technological characteristics of the meat filling systems.

The investigated technological properties of the beef minced meat make it possible to consider the rational mass fraction of a food additive on the basis of Fe_3O_4 nanopowder (“Magnetofood”) of 0,10 % to the meat mass.

Conclusion

The results of the sensory analysis of beef minced meat with the addition of the food additive based on Fe_3O_4 nanopowder (“Magnetofood”) showed the improvement in the sensory characteristics of the experimental samples of the beef minced meat – the average score for sensory indicators increased by 1,0–1,2 points compared to the control.

The losses reduction during the heat treatment of chilled minced meat with addition of 0,05 – 0,15% Fe_3O_4 by 14,4–18,4% was established due to the ability of Fe_3O_4 nanoparticles to the electrostatic and coordination interaction with proteins of the minced meat systems [29, 39, 40]. This leads to a change in the moisture content in the experimental samples of the beef minced meat for the increasing in the water-holding capacity of minced meat and better distribution and content of H_2O and, as a result, a decrease in losses during the heat treatment.

It is proved that the addition of 0,05–0,15% to the food additive on the basis of the Fe_3O_4 nanopowder (“Magnetofood”) has a positive effect on the functional and technological properties of minced beef. In particular, in the experimental samples of the fresh minced meat there is a gradual increase in all functional and technological indicators with an increase in the mass fraction of Fe_3O_4 compared to the control: the WHC increases by 1,1% – 2,0%; FRC – 1,2–2,6%; EC – 1,3–2,0%; ES – 1,4–2,1%.

Similar dynamics and in the experimental models of the chilled beef from beef after 24 hours of storage at $5^\circ\text{C} \pm 1^\circ\text{C}$ only in all cases of their value dropped by 1,3% to 2,0% compared to freshly prepared minced meat.

This is probably due to the surface-active sorption, the complex-forming properties of ionized nanoparticles of the food additive “Magnetofood”, as well as its affinity with protein molecules [39, 40]. Therefore, the introduction of the food additive based on Fe_3O_4 nanopowder (“Magnetofood”) to the minced meat increases the level of moisture and fat and the formation of the stable minced emulsions, in particular, with the lipid and protein components of minced meat systems.

The microbiological characterization of prototypes of the chilled beef from beef showed that the introduction of food additives on the basis of the Fe_3O_4 nanopowder (“Magnetofood”) in the amount of 0,05–0,15% by weight of the meat after 24 hours storage reduces the level of total microbial contamination from $6,2 \times 10^5$ CFU/g in control to $(5,1 – 5,8) \times 10^5$ CFU/g in the samples enriched “Magnetofood”, that is, 6,5–19,6%.

The positive influence of the dietary additives on the basis of Fe_3O_4 nanopowder (“Magnetofood”) on the structural and mechanical properties of the minced meat from beef:

1) the shear stress reduction limit to 26% compared to the control sample, i.e. the beef minced meat with the introduction of the food additive Fe_3O_4 has a softer and gentler consistency than the control;

2) the stickiness increasing of the minced meat by $(0,15–0,25) \times 10^4$ PA. Moreover, with the mass fraction increase of Fe_3O_4 nanopowder (“Magnetofood”) stickiness of the minced meat increased 1,16–1,42% compared to control.

This is probably connected with the activation of intracellular enzymes due to their interactions of ionogenic groups of the components of the minced meat with the polarized nanoparticles of the food additives on the basis of the Fe_3O_4 nanoparticles (“Magnetofood”) and the formation of complexes “boolen matrix enzyme – Fe_3O_4 nanoparticles” [38, 39].

The rational mass fraction of food additives on the basis of Fe_3O_4 nanopowders (“Magnetofod”) is established, which provides the best complex of technological properties of forage systems and the smallest losses in heat treatment, it is 0,10% to the mass of meat.

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Chemical composition of fenugreek hay leaves

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Abstract

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Introduction. It was researched the chemical composition of fenugreek hay leaves which is a source of biologically active substances and used as spice-aromatic raw materials for the confectionery products.

Materials and methods. The chemical composition of fenugreek hay leaves were studied by ultra high-speed high performance liquid chromatography, spectrophotometry and gas chromatography with mass-selective detection. To investigate the composition of leaves extract aglycones acidic hydrolysis was used. After hydrolysis aglycones were extracted by ethylacetate and extracts were used for chromatography. To identify component composition the derivatization method was used.

Results and discussion. The presence of phenolic compounds, phenolcarboxylic acids, chlorophylls, trigonoline alkaloids, which have a high antioxidant potential, was confirmed in the chemical composition of fenugreek leaves. It is known that phenolic compounds in plants are rarely found in the free state. Most of them are presented in the form of various O- and C-glycosides. The diversity of flavonoid glycosides is due to a significant amount of sugars and the different positions of their attachment to the aglycones, as well as the fact that sugars may have different configurations of glycosidic bonds.

It was identified the fructose, beta-D-arabinopyranose, sucrose, raffinose, glycerol, xylitol in the fenugreek leaves extracts. The presence of amino acids such as L-alanine, L-valine, L-proline, L-threonine had been proved in these leaves. The oxalic, succinic, 2,3-dioxopropanoic, 2,3,4- trihydroxybutyric acids and fatty palmitic and alpha-linolenic acids were also identified in the leaves extracts.

Fenugreek essential oil contains: hexadecene, eicosanol, ethyl palmitate, ethyl linoleate, beta-hydroxy-butyrac, beta-aminoisobutyric, hydroxybutanedioic, 1,2,3-propanethreocarboxylic acids; ethyl esters of linoleic, levulinic, palmitic, ethylpalmitic, citric acids, which are likely to form a flavor of spicy-aromatic raw materials.

Conclusions. The presence of phenolic compounds, essential nutrients, aromatics in the fenugreek leaves should increase the shelf life, the nutritional value, improve the sensory properties of confectionery.

Introduction

Food manufacturers, in particular confectionery products, are increasingly using spice-aromatic plant raw materials as a source of biologically active substances (BAS). Essential oils, tannins and phenol substances play an important role in the formation of the flavor, promote the increase of the product shelf life. Besides, bioactive substances of medicinal plant can prevent cardiovascular diseases, carcinogenesis, inflammation, atherosclerosis and other human diseases [1, 2].

Leafy vegetable Fenugreek (*Trigonella foenum-graecum*) has been used as an effective medicinal plant as well as a fodder plant. Leaves of fenugreek hay have the aroma and antioxidant properties and pleasant taste [3-6]. It was shown that the green leaf of *Trigonella foenum-graecum* influenced the cholesterol balancing, sugar-level, skin inflammation (wounds, rashes, boils), treating arthritis, asthma, sore throat [9]. It was suggested that phytoconstituents such as flavonoids, alkaloids, terpenoids, steroids, saponins, anthocyanin, tannin and other were involved in this effect.

Fenugreek is an annual spice-aromatic plant, belongs to the legumes family. Seeds and leaves of plants contain many antiseptic, antioxidant and anti-inflammatory substances, such as apigenin, genistein, campeferol, quercetin, rutin, selenium, trihonellin alkaloid, iodine and are using in the food industry [7, 8]. The foliage contain a large amount of bioactive substances: vitamins A, C, B1, B2, B9 (folic acid), nicotinic acid (vitamin PP), rutin, tannins, food fibers, macro and microelements – iron, potassium, phosphorus, magnesium, calcium etc. [10–14].

Phenolic compounds present in plants are rarely found in a free state. Most of them are presented in the form of various O- and C-glycosides. The variety of flavonoid glycosides is due to a significant amount of sugars (glucose, arabinose, xylose, etc.) and the their ability to attach to the position of aglycones, as well as sugars can have different configurations of glycoside bonds. To the best of our knowledge, there were not sufficient data on the composition of carbohydrates, amino acids, fatty acids, aromatic substances of fenugreek hay leaves in the scientific literature, and this substantiates the actuality of the present work.

Consequently, the identification and quantification of phenolic compounds in plant material requires complex researches.

The purpose of this work was to study the chemical composition of the leaves of fenugreek hay, the possibility of its use in the production of a new range of flour confectionery products with high fat content, in particular, crackers and puffy cookies, as a natural antioxidant and a flavoring additive. The presence of antioxidants in the formulation of foods with fat content is very important because they can inhibit the rate of fat oxidation [15]. To determine the classes of organic substances of fenugreek leaves the high-performance liquid chromatography was used.

Materials and methods

The samples of fenugreek (*Trigonella foenum-graecum*) leaves have been received from M.M. Grishko National Botanical Garden of National Academy of Sciences of Ukraine.

Ethanol extract obtaining

2.5 g of dry crushed leaf was putted to a 100 ml flask, 60 ml of 96% ethanol was added, reversed condenser was attached and flask was heating in a boiling water bath for 90 min. After that, the water bath was cooled, the fridge was washed with 5 ml of ethyl alcohol, and the content of the flask was filtered into a 100 ml measuring flask. Then procedure was repeated with 35 ml of ethanol. The final volume of ethanol extract was adjusted to 100 ml.

Obtaining of hydrolyzed extracts

0.4 g of dry crushed leaves were transferred to a 100 ml flask attached by a reversed condenser, 20 ml of ethyl alcohol, 20 ml of distilled water and 10 ml of concentrated hydrochloric acid were added. After attaching the flask to the reversed condenser the mixture was heated for 90 minutes in a boiling water bath. After that, the condenser was washed with 20 ml of distilled water and flask was cooled. The content of the flask was transferred to a 100 ml separate funnel through a paper filter, 25 g of sodium chloride was added and mixed thoroughly. The organic compounds were extracted with 30 ml of ethyl acetate, the procedure was carried out in two consequent repetitions. After extracts drying with anhydrous sodium sulfate, the ethyl acetate was evaporated by vacuum. After evaporation the residue was dissolved in 50 ml of ethanol.

Ultra high-speed high performance liquid chromatography

Ultra high-speed high performance liquid chromatography of leave extracts was carried out using HPLC (WATERS (USA), column ACQUITY UPLC®BEHC₁₈, 1,7 μm, 50x2,1 mm) with diode-matrix detection (PDA) and gradient changing of the mobile phase (acetonitrile-water) composition.

Organic substances with hydrogen mobile atoms in plants are present in conjugated form and to investigate their composition in forms of aglycones acidic hydrolysis was used. After hydrolysis aglycones were extracted by ethylacetate and extracts were used for chromatography. Composition of remaining ethanol extracts after removal of ethanol were also analyzed [10].

Spectrophotometric analysis

Spectrophotometric analysis of leave extracts was performed on the spectrophotometer Specord 210 Plus (Germany) [16].

Gas chromatography with mass-selective detection

To identify component composition of the extracts, the derivatization method was used, which allows to increase the molecular weight of the initial substances. N-methyl-N-trimethylsilyl-trifluoroacetamide (TMS) reagent was used for derivatization.

For TMS derivatives obtaining 5 ml of ethanol extract was putted into vial and ethyl alcohol was removed by evaporation at 78° C. 300 μg of anhydrous pyridine and 100 μg of TMS reagent were added to the dry residue. Vial was sealed and placed in UZB for 30 minutes. After this, 1 ml of acetonitrile was added to the vial, mixed and obtained mixture of derivatives were analyzed on chromatograph Agilent GC/MSD 7890A/5975C with capillary column HP-5MS [13].

Results and discussion

According to electronic absorption spectrum of the samples the phenolic acids (absorption at 326 nm), aromatic compounds (absorption in the range 350-600 nm), chlorophylls (667 nm) were presented in initial leaf extracts of fenugreek (Figure 1).

Displacement of the maxima to the ultraviolet region with an increase of the pH of the solution (Figure 1, 2) indicates the destruction of the intramolecular hydrogen bond under pH increasing.

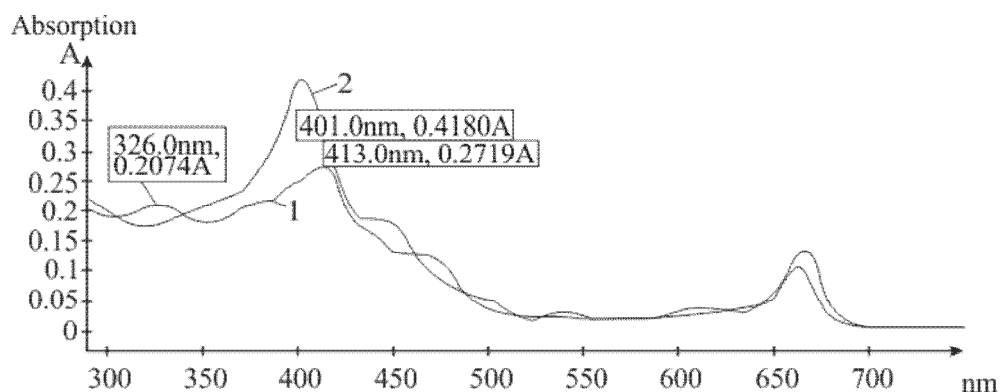


Figure 1. Electronic absorption spectrum of initial leaf extract (1-pH=6,5; 2-pH=11,8)

Ultra high-speed high performance liquid chromatography (UHPLC) of initial leaf extracts (Figure 2a and 2b) have demonstrated presence of phenol carboxylic acids (retention time 4.52, 5.59, 6.46 min), catechins (retention time 5.24, 5.45 min) and alkaloid trihonellin (retention time 6.29 min). Eight different substances were identified by this analysis with spectrophotometrical detection at 325.0 and 350 nm (Table 1).

Table 1

Content of substances in initial leaf extract according to Figure 2 a, b

Retention time, min	% from the total content	Retention time, min	% from the total content
PDA 325.0 nm		PDA 350.0 nm	
0,983	7,7	5,241	4,8
4,520	54,9	5,454	17,3
6,461	37,5	5,585	47,0
-	-	5,830	18,0
-	-	6,292	13,0

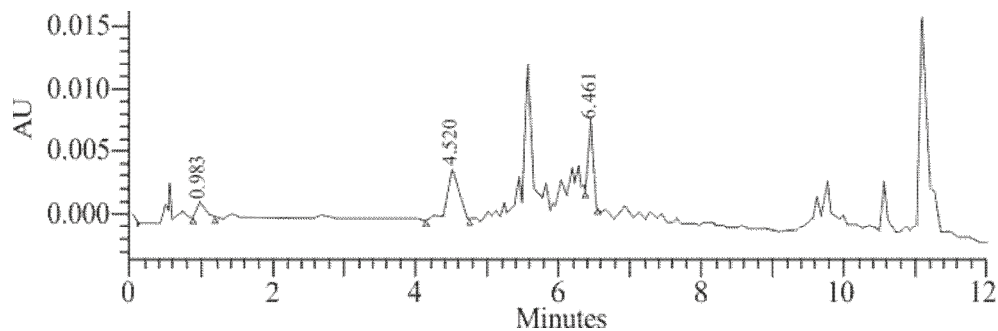


Figure 2a. Chromatogram of initial leaf extract (PDA 325.0 nm).

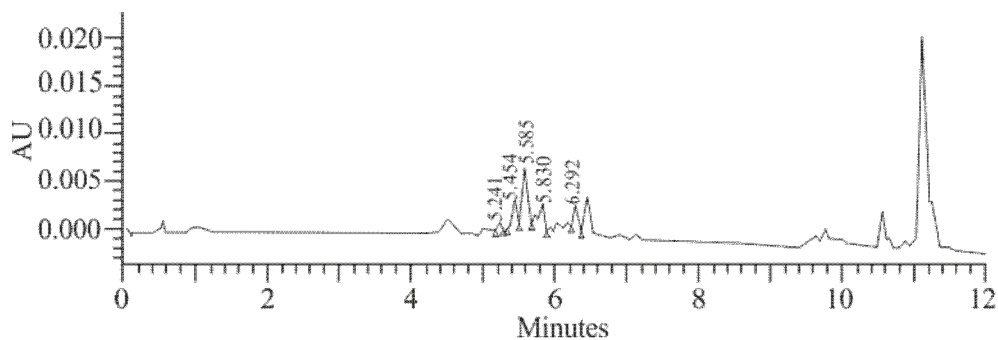


Figure 2b. Chromatogram of initial leaf extract (PDA 350.0 nm).

The distribution of peaks and their absolute intensity on the sample electronic absorption spectrum after acid hydrolysis were similar to the original spectrum (Figure 3).

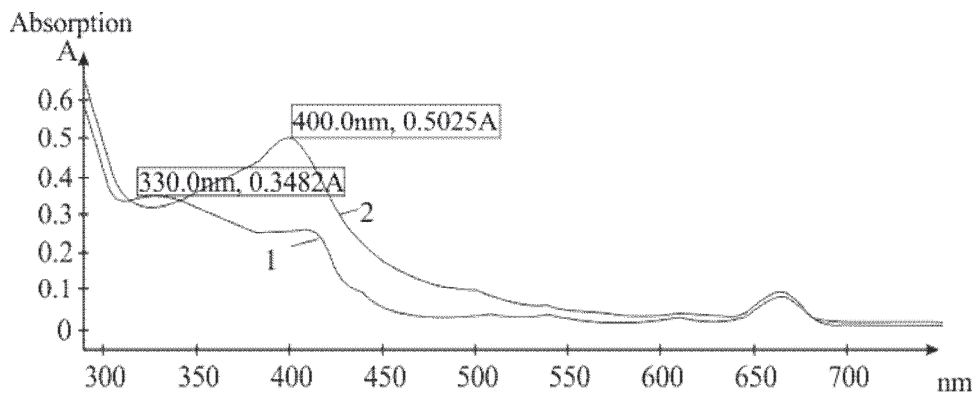


Figure 3. Electronic absorption spectrum of ethylacetate extracts after hydrolysis of leaf extracts (1-pH=6,5; 2-pH=11,8)

Analysis of this extracts by HPLC had shown that catechins were destructed under acid hydrolysis of initial leaf extract (Figure 4). Trihonellin was absent in ethylacetate extracts of hydrolyzed initial leaf extracts. The number of new substances were detected after acid hydrolysis, absorbtion peaks of which are close to phenolic acids. Ratio of detected components are presented in Table 2.

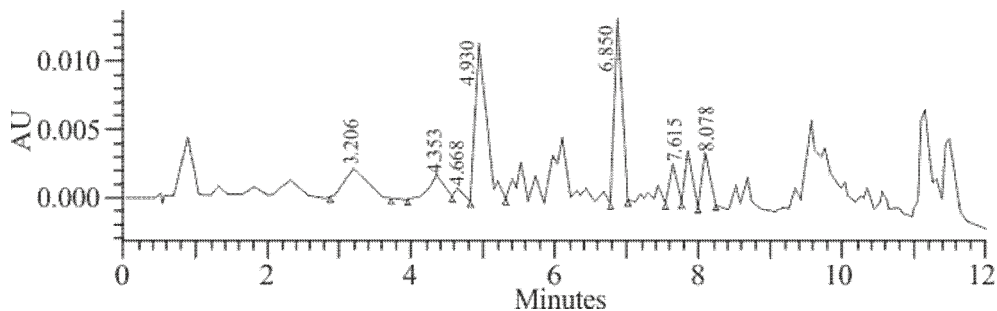


Figure 4. Chromatogramm of ethylacetate extracts after hydrolysis of leaf extracts (PDA 350)

Table 2
Ratio of components ethylacetate extracts after hydrolysis of leaf extracts (PDA 350.0 nm)

№	Retention time, min	% from the total content
1	3,206	14,84
2	4,353	6,65
3	4,668	1,30
4	4,930	36,90
5	6,859	25,02
6	7,615	5,66
7	8,078	9,63

Using of mass-chromatography for analysis of initial leaf extracts gave possibility to detect number of aliphatic substances mainly hexadecen, linolenic acid and eycosanol (Figure 5).

The mass-chromatogramm of ethylacetate extracts after hydrolysis of leave extracts presented in Figure 6 have demonstrated that after acid hydrolysis, a number of compounds appeared: ethyl esters of levulinic acid, ethyl palmitate, ethylinoleate.

The mass-chromatography of ethylacetate extracts after hydrolysis has detected the carbonic acid esters, that are probably the constituent of essential oil of fenugreek. They are the ethyl esters of levulinic acid, ethyl esters of citric acid, 1,2,3-propanetricarboxylic acid ethyl esters, ethyl esters of palmitic, linoleic, beta-hydroxy-butyric and citric acid.

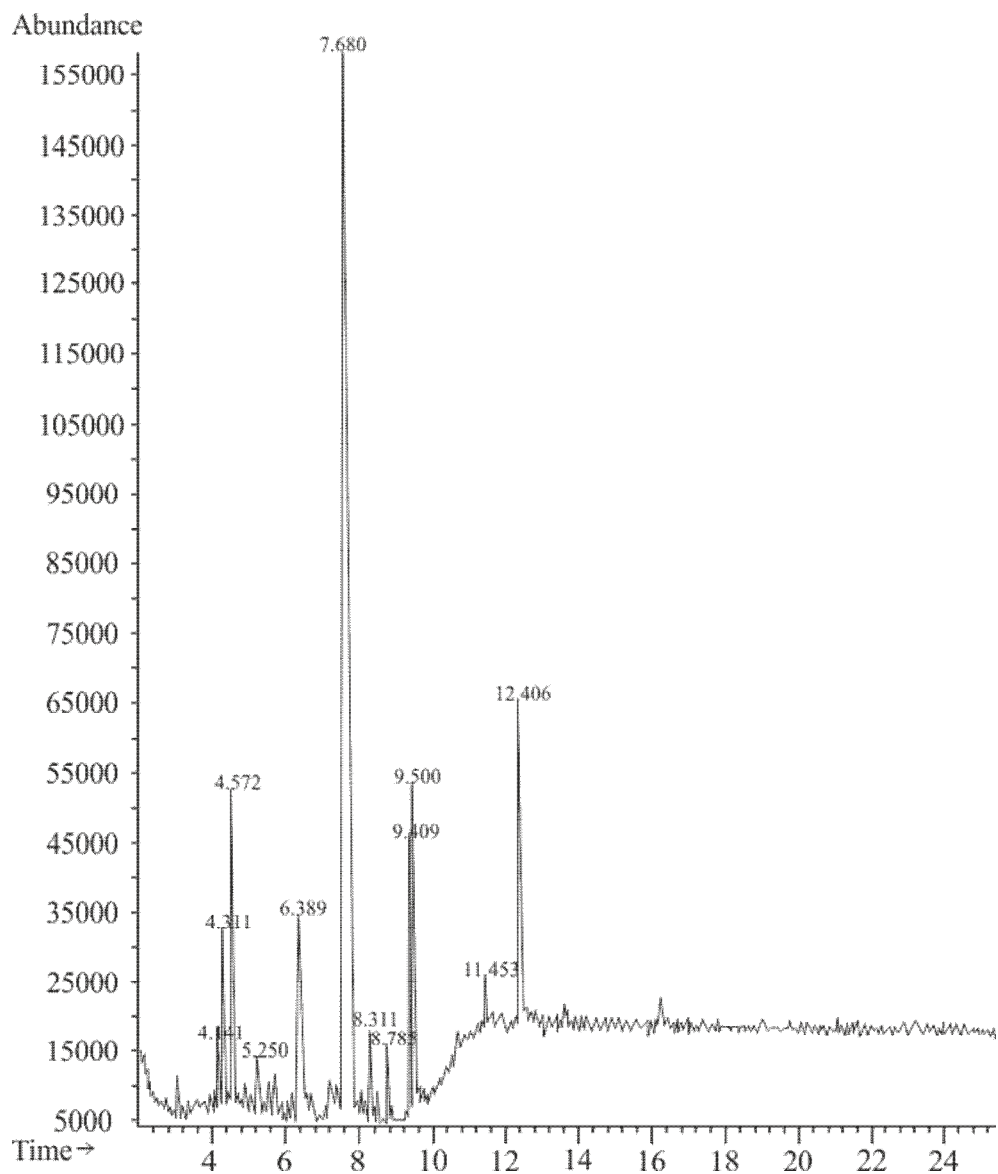


Figure 5. Mass-chromatogram of initial fenugreek leaf extracts

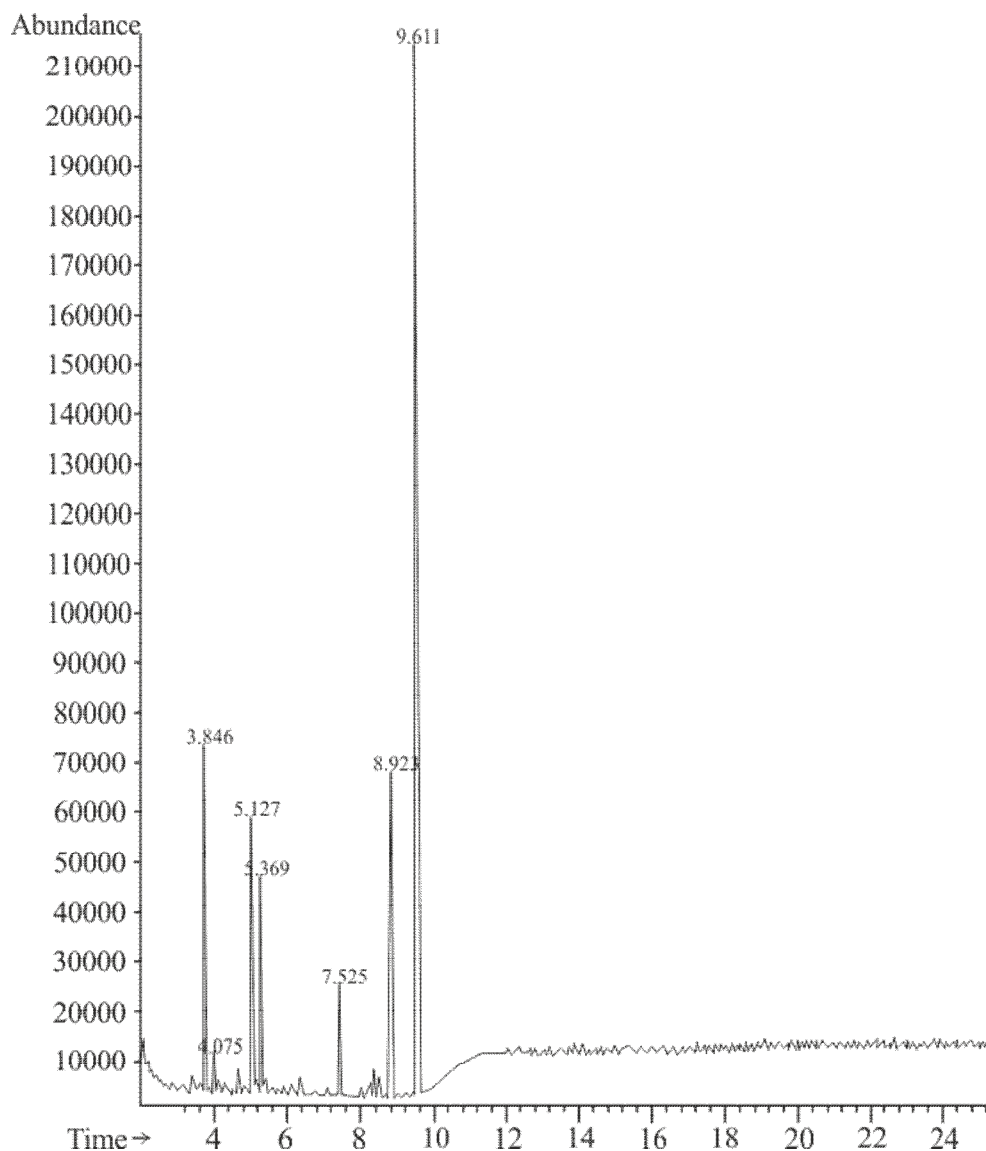


Figure 6. Mass-chromatogramm of ethylacetate extracts after hydrolysis of fenugreek leaf extracts

To identify component with low molecular weight derivatization method was used and amino acids L-alanine, L-valine, L-proline, L-threonine, a number of carbohydrates, mainly lyksosa, β -dl-arabinopyranose, sucrose and raffinose were detected in initial fenugreek leaf extracts (Figure7). The oxoacetic acid, succinic acid, 2,3-dioxypropane acid, 2,3,4 – trihydroxybutyric acid, palmitic acid, α -linolenic acid, as well as glycerol and xylitol were identified in these extracts after derivatization.

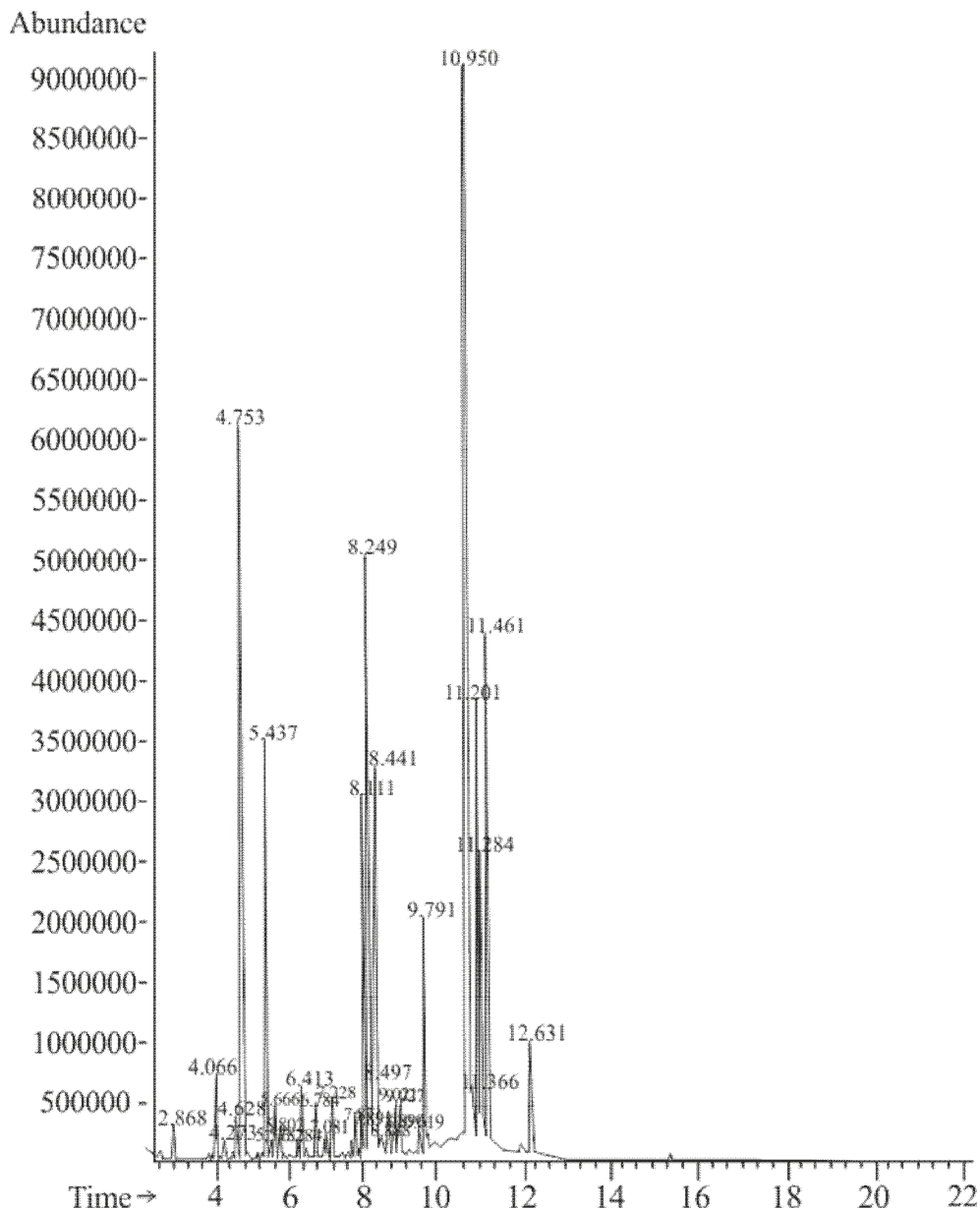


Figure 7. Mass-chromatogramm of TMS derivatives of initial ethanol extracts of fenugreek leaf

The TMS derivatives of constituents of fenugreek leaf extracts were obtained also after acidic hydrolysis. Mass-chromatogramm of TMS derivatives of fenugreek leaf extracts after acidic hydrolysis have demonstrated presence of β -hydroxybutyric acid, beta-aminoisobutyric acid, hydroxybutanedicarboxylic acid, citric acid, ethyl ester of palmitic

and linoleic acid (Figure 8). The intense (2,499 min) peak is due to the interaction of the destruction product of the reagent (methylamine) with the reagent.

Therefore, using ultra high-speed high performance liquid chromatography, spectrophotometry, gas chromatography with mass-selective detection it was shown the presence of phenolic carboxylic acids, flavonoid compounds, trihonellin alkaloids, which have a high antioxidant potential, the components of fenugreek essential oils, sugars, amino acids and aromatic substances in fenugreek leaf.

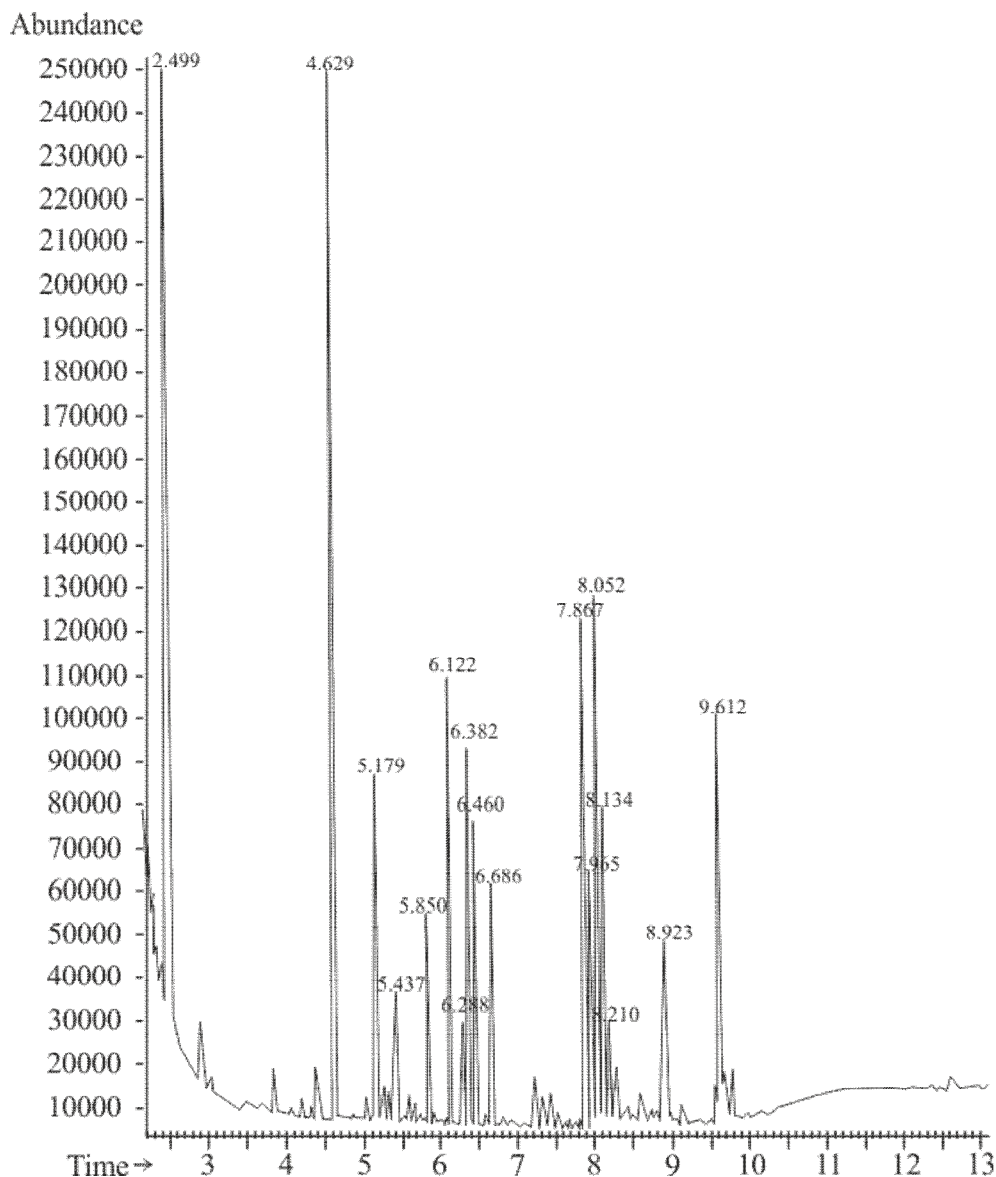


Figure 8. Mass-chromatogramm of TMS derivatives of fenugreek leaf extracts after acidic hydrolysis

Conclusion

1. For the first time by application of spectrophotometry method with reference to electronic absorption spectrum we were able to identify the phenolic acids (absorption at 326 nm), aromatic compounds (absorption in the range 350–600 nm), chlorophylls (667 nm) in initial leaf extracts of fenugreek.

2. By conducting analysis of this extracts by HPLC it was shown destruction of catechins and absent of trihonellin in ethylacetate extracts. New identified substances judging from absorption peaks are close to phenolic acids.

3. Mass-chromatography allowed us to recognize in fenugreek leaf extracts after acid hydrolysis a number of compounds: ethyl esters of levulinic acid, ethyl palmitate, ethylinoleate. However, alongside we found carbonic acid esters, that probably corresponds as constituent of essential oil of fenugreek. In addition we found number of carbohydrates and complex phenolic carboxylic acids, flavonoid compounds, trihonellin alkaloids, which have a high antioxidant potential. It is recommended the using of fenugreek leaf as effective source of antioxidants in production of the flour confectionery products, particularly of crackers and puffy cookies.

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Changes in cholesterol and free fatty acid content of Kars Gravyer Cheese (A Turkish dairy product produced by the traditional method)

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Abstract

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Introduction. This study was carried out to determine changing in the ratio of free fatty acids and cholesterol depended on the maturation period of Kars Graiver cheese produced in the traditional way, and the affect of the duration of maturation on the fatty acids composition and cholesterol levels.

Materials and methods. The fat content of the cheese samples was determined by Gerber's method. Flame Ionization Detector–Gas Chromatography (GC/FID) was used to determine the fatty acids composition and cholesterol content.

Results and discussion. It was found the fat content of Kars Gravyer Cheese samples was between 27.0–38.50%. The cholesterol content in the cheese samples ranged from 45.70 to 55.80 mg/100g during 90 days of maturation. In Kars Gravyer Cheese samples, 16 saturated and unsaturated fatty acids were identified. In Gravyer Cheese samples, the content of volatile fatty acids (Butyric acid and myristic acid) increase up to 25th day ($P < 0.01$) and decrease from 45th day to 90th day. While levels of free fatty acids (palmitic acid and linoleic acid) generally decrease to 25th day, they begin increasing again until the end of the maturation period. In the 90 days period of storage of Kars Gravyer Cheese, palmitic, oleic, myristic and stearic acids were found to constitute 74.29% of the total free fatty acids content. In the samples studied, the most abundant saturated fatty acids were identified as palmitic and stearic acids. Oleic acid was found to be the most abundant unsaturated fatty acid. In cheese samples, the content of monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) ranged 28.38–32.37% and 1.59–1.84%, respectively. In Kars Gravyer Cheese sample, the Atherogenicity (AI) index was defined as 2.57–3.04.

Conclusion. Fatty acids are precursors of aroma compounds like short and medium chain free fatty acids, ethyl ketones, esters and thioesters, formed in cheese in a result of various biochemical processes. The detection of large amounts of fatty acids with short and medium chains in Gravyer Cheese samples providing aroma, indicate that this cheese is flavorful cheese.

Introduction

Today there are about 4000 different varieties of cheese in the world with different aroma and textural properties [1]. The most important factors affecting cheese quality are flavor and aroma of cheese, texture, and appearance. Unique characteristic properties of cheese are formed by biochemical reactions such as glycolysis, proteolysis, and lipolysis occurring during maturation. Free fatty acid (FFA), which emerges as a result of lipolysis reaction, is effective on the flavor and aroma of cheese. FFA is an important, volatile precursor of catabolic reactions, producing compounds that contribute to aroma [2]. The presence of short, medium and long-chain fatty acids is considered the most important indicator of cheese maturation after the compounds formed by glycolytic and proteolytic reactions [3].

The amount of free fatty acids in dairy products has potential effects not only on the taste and texture of dairy products but also on nutrition and health as antimicrobial agents. Determination of fatty acid profile of cheese is also important in terms of these negativities [4]. Cheese, which is an important source of fat in human nutrition, contains a high level of various fatty acids. From a nutritional point of view, different types of cheese contain a high level of digestible fat. Its digestibility is in the range of 88–94% [5]. However, cheese is usually presented with a negative nutritional image due to the relationship between saturated fatty acids (SFA), the main fatty acids of cheese, and cholesterol, leading to cardiovascular diseases. Although many researchers view SFA as one of the contributing factors in heart disease, there has been no direct link between cardiovascular disease and milk fat, or a real study indicating dairy products' role in heart disease [6]. Cheese is a rich source of some trans-fatty acids and short-chain fatty acids that can be considered as part of a healthy diet [7]. The World Health Organization and the American Heart association have advised that consumers limit their intake of saturated fatty acids and cholesterol to prevent coronary heart disease. The reduction of cholesterol level in dairy products will be an attractive alternative to satisfy consumer's concerns and demands [8]. Gravyer cheese is one of the few European-style cheese that has economic value and is appreciated by consumers like domestic cheese varieties in Turkey [9]. Gravyer Cheese, one of the 18 varieties of cheese that is economically important in the world, is in the same group as Emmental (Switzerland), Gruyere (France), Fontina (Italy), Samsø (Denmark), Gouda and Edam (Netherlands) [10]. Approximately 90% (544 tons) of the production of Gravyer, which is mostly produced in the Eastern Anatolia Region especially in Kars Province and its surroundings, is carried out in Kars [11]. The industrial production of Kars Gravyer Cheese is quite low. Production is mostly carried out by traditional methods in dairy farms [12]. Gravyer Cheese is produced in and around Kars Province and takes the first place after kashar, tulum and white cheese production. It has economic value for the people of the region and Kars Gravyer Cheese has brand awareness throughout the country [9].

Although there are many studies on the fatty acid composition and cholesterol content of various cheeses, no studies have been conducted on the determination of changes in cholesterol and fatty acid content during the production and maturation of Kars Gravyer Cheese. However, there are few studies in which the chemical and microbiological properties of Kars Gravyer Cheese, bought from a point of purchase, are revealed [9,13]. Therefore, the aim of this study is to determine the fatty acid composition and cholesterol level of Kars Gravyer Cheese, which will be produced by traditional methods in dairy conditions, and to determine the effect of different maturation periods on fatty acid composition and cholesterol level.

Materials and methods

Sample preparation

Gravyer cheese was produced in a dairy farm in central Boğatepe village of Kars Province according to the flow diagram given in Figure 1. Gravyer cheese production was done in two repetitions. Samples were taken on different maturation days (0th, 10th, 25th, 45th, 60th and 90th days) from the produced cheeses and brought to the laboratories under cold chain conditions and fat content, fatty acid composition and cholesterol analyses were performed.

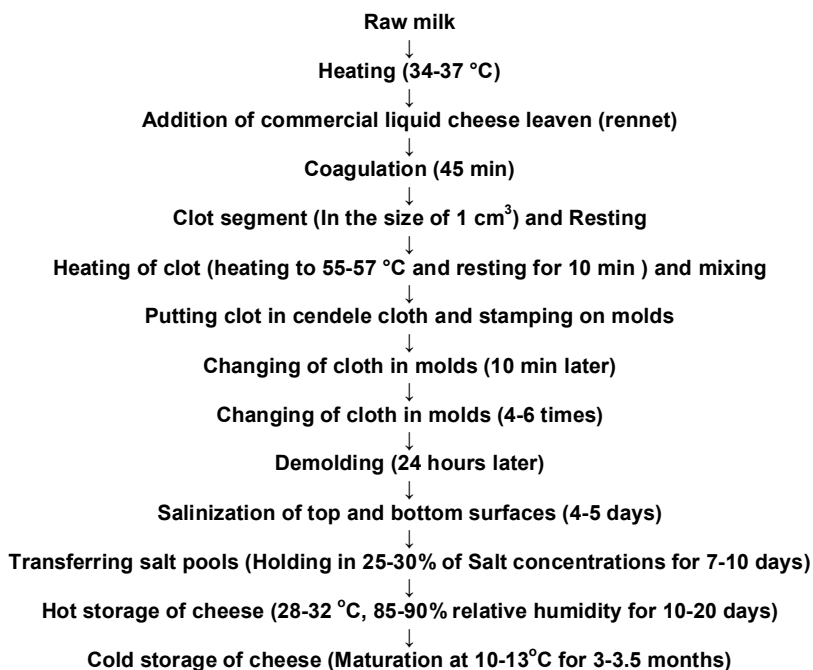


Figure 1. Production flowchart of Gravyer cheese

Methods

Determination of fat

The fat content of the samples was determined using Gerber method [14].

Determination of fatty acid composition

The fatty acid composition of the samples was determined according to the fatty acid methyl ester method (FAME) (AOAC 1996.01) [15]. Approximately 0.1 g of fat obtained as a result of fat determination method was mixed and shaken with 10 ml of n-hexane and mixed again with a 0.5 ml 2 N potassium hydroxide solution with methanol. After standing for 1-2 hours in the dark, 1 µl of the supernatant was taken and directly injected into the gas chromatograph.

GC Conditions for the analysis of fatty Acid composition

For the fats, the FAME composition was analyzed using a Restek RTX-2330 capillary column (60 m, 0.25 mm id, 0.1 µm film thickness, Bellefonte, PA, USA) in Shimadzu brand gas chromatography (model QP2010 Plus) and a flame ionization detector. The device was given 1 µl as the injection volume from the sample. The column furnace temperature was programmed to reach 240 °C with an increase of 4 °C/min after kept for 3 minutes at 100 °C and to wait 18 minutes at the last temperature value. The injection temperature was set at 250 °C and the detector temperature was set at 255 °C. Helium was used as a carrier gas. Injection split ratio was used at 1:80 ratio. For the control of the GC/FID system, the LabSolution computer program and FAME Mix standard (37 components) (Restek) were used. FAME peaks were identified by comparing the chain lengths and retention times of the fatty acids specified in the FAME standard.

Determination of cholesterol level

Cholesterol analysis of samples was done according to [16] with some modifications. According to the method, 1 ml of internal standard (stigmaterol, 0.5 mg/ml) and 0.5 ml of 2 N alcoholic potassium hydroxide solution were added to 0.5 g of fat and the mixture is left to stand in a water bath at 80 °C for 15 minutes. Then, after cooling to room temperature, 1 ml of distilled water and 5 ml of n-hexane were added to it and shaken for 1 min. it was then centrifuged at 2000 g for 1 min and 1 mL of the supernatant was removed and injected directly into the gas chromatography device.

GC Conditions for cholesterol analysis

Cholesterol analysis of samples was performed on a Shimadzu brand gas chromatography (model QP2010 plus) device using Restek Rtx-65TG (30 m x 0.32 mm ID, film thickness 0.1 µm) (Restek international, Bellefonte, PA, USA) silica column (65% diphenyl—35% dimethyl-polysiloxane) and flame ionization detector (FID). The column oven temperature was raised to 150 °C with an increase of 30 °C/min and then to 360 °C with an increase of 15 °C/min and kept at this temperature for 3 minutes. Injection port temperature was set at 300 °C and detector temperature was set at 370 °C, helium was used as the carrier gas. The injection split ratio was used at 1:25.

Lipid quality index

Unsaturated/saturated fatty acids (USFA / SFA) ratios and desired fatty acids (DFA) were calculated from the fatty acid profiles of the cheeses.

In addition, in order to correlate the fatty acids profile with the risk of cardiovascular disease, the atherogenicity indices (AI) were calculated according to the following equation suggested by the equation by [17].

AI, shows the relationship between the sum of the main saturated FAs and the main classes of unsaturated FAs. The former is considered as proatherogenic (favouring the adhesion of lipids to cells of the immunological and circulatory system), and the latter as anti-atherogenic (inhibiting the aggregation of plaque and diminishing the levels of esterified fatty acid, cholesterol, and phospholipids, thereby preventing the appearance of micro-and macrocoronary diseases) [18].

Statistical analysis

In the evaluation of the obtained results, mean values and standard errors of the samples were determined using SPSS package program, and differences in the fatty acid composition and cholesterol level between fresh and mature Gravyer Cheese samples were analyzed by t-test.

Results and discussions

Fat ratios of Kars Gravyer Cheese samples are given in Table 1 and cholesterol ratios in Table 2.

Table 1

Fat proportion of Kars Gravyer Cheese during ripening ($\bar{x} \pm S_x$)

Parameter (%)	Ripening Period (Day)						F value	P
	0	10	25	45	60	90		
Fat	27.0 ±0.00a	28.0 ±0.51b	29.5 ±0.70c	33 ±0.71d	35.57 ±0.72e	38.5 ±0.71f	789.97	***

Results are expressed as mean ± standard deviation of means

*** a,b,c,d,e,f. : Different letters in the same line refers significant differences between the averages ($P < 0.001$)

Table 2

Cholesterol level of Kars Gravyer Cheese during ripening (mg /100g)

Ripening period (Day)					
0	10	25	45	60	90
45.70	48.54	58.36	155.80	104.72	101.52
±3.18	±6.32	±9.27	±6.32	±16.51	±0.89

Depending on the type of cheese, ripening time varies from a few weeks to three years. The cholesterol ratio of cheese samples ranged from 45.70 to 155.80 mg /100g during 90 days of maturation. Health lipid indices and the ratio double-carbon saturated of and unsaturated fatty acids in Kars Gravyer Cheese samples is given in Table 3–5.

Table 3

Health lipid indices of Kars Gravyer cheese (mg /100 g)

Fatty Acids	Kars Gravyer cheese*						Total
	0	10	25	45	60	90	
Saturated fatty acid	98.22	98.45	98.56	98.44	98.36	98.49	410.93
SCSFA C4:0-C8:0	5.35	6.12	6.15	5.90	5.63	4.84	33.99
MCFA C10:0-C14:0	17.34	19.47	19.24	18.48	17.59	15.95	108.07
LCSFAC 16:0-C18:2	75.53	72.86	73.17	74.06	75.14	77.70	448.46
MUFA	30.15	28.38	28.59	29.97	32.37	31.30	180.76
PUFA	1.84	1.84	1.84	1.76	1.80	1.59	10.64
DFA	45.52	43.46	44.16	45.31	47.98	48.05	274.48
AI	2.79	3.04	3.01	2.83	2.57	2.71	16.95
USFA/SFA	0.47	0.43	0.44	0.46	0.49	0.46	2.75

*Data were presented as average values; AI – atherogenicity index;

Table 4
Changes in saturated fatty acid content (mg/100g) during ripening of Kars Gravyer cheese

Saturated fatty acid	Ripening period (Day) ripening ($\bar{X} \pm S_x$)								F Value	P
	0	10	25	45	60	90				
Butyric acid (C4:0)	2.56±0.20 a	2.71±0.04 b	2.74±0.10 b	2.70±0.05 b	2.58±0.01 b	2.64±0.36 b	22.23	***		
Caproic acid (C6:0)	1.72±0.23 bc	2.04±0.02 d	2.03±0.06 cd	1.95±0.14 cd	1.86±0.01 cd	1.46±0.07 ab	10.32	**		
Caprylic acid (C8:0)	1.07±0.15	1.37±0.01	1.38±0.02	1.25±0.17	1.19±0.02	0.74±0.34	3.49	> 0.05		
Capric acid (C10:0)	2.55±0.59 ab	3.18±0.02 bc	3.15±0.01 bc	2.90±0.40 abc	2.71±0.17 abc	2.17±0.16 a	3.98	*		
Lauric acid (C12:0)	3.10±0.65	3.72±0.04	3.64±0.03	3.46±0.40	3.24±0.02	2.67±0.17	3.51	> 0.05		
Myristic acid (C14:0)	11.69±0.96 b	12.57±0.08 a	12.45±0.31 a	12.12±0.79 a	11.64±0.02 a	11.11±0.35 a	8.69	**		
Pentadecanoic acid (C15:0)	1.72±0.34	1.47±0.02	1.48±0.01	1.57±0.11	1.60±0.01	1.45±0.31	1.01	> 0.05		
Palmitic acid (C16:0)	29.10±1.03 a	28.61±0.04 b	28.27±0.08 b	27.98±0.85 b	27.73±0.07 b	29.81±0.99 b	7.40	**		
Heptadecanoic acid (C17:0)	0.91±0.23	0.79±0.03	0.74±0.01	0.77±0.02	0.82±0.04	0.97±0.01	1.80	> 0.05		
Stearic acid (C18:0)	13.53±0.43 a	13.24±0.2 b	13.73±0.18 b	13.58±0.55 b	13.81±0.02 b	15.16±0.25 b	11.87	**		

Results are expressed as mean ± standard deviation of mean

*** a,b,c,d; Different letters in the same line refers significant differences between the averages ($P < 0.001$, $P < 0.01$)

Table 5

Changes in unsaturated fatty acid content (mg/100g) during ripening of Kars Gravyer cheese

Unsaturated fatty acid	Ripening period (Day) ($\bar{X} \pm S_v$)						F Value	P
	0	10	25	45	60	90		
Myristoleic acid (C14:1)	0.91±0.05 b	0.90±0.01 b	0.86±0.01 b	0.92±0.02 b	0.88±0.01 b	0.66±0.12 a	84.82	***
Palmitoleic acid (C16:1)	1.92±0.41 a	1.72±0.01 b	1.77±0.12 b	1.73±0.08 b	1.78±0.01 b	1.64±0.28 b	16.32	**
Oleic acid (C18:1n9c)	23.12±3.68 a	20.22±0.28 b	20.19±0.03 b	21.29±1.64 b	22.05±0.04 b	22.91±0.03 b	58.38	***
Elaidic acid (C18:1n9t)	4.20±2.53a	5.54±0.12 b	5.77±0.12 b	6.03±0.70 b	6.27±0.11 b	4.96±0.19 b	9.53	**
Linoleic acid (C18:2 n6c)	0.42±0.01	0.41±0.01	0.43±0.04	0.33±0.14	0.41±0.01	0.46±0.05	0.88	> 0.05
Cis-11 - eicosenoic acid (C20:1)	1.42±0.00	1.43±0.01	1.41±0.02	1.43±0.04	1.39±0.03	1.13±0.29	1.90	> 0.05

Results are expressed as mean ± standard deviation of mean

*** a,b,c,d. ; Different letters in the same line refers significant differences between the averages (P<0.001, P<0.01)

Cheese ripening is a slow and complex biochemical process that is costly due to the long storage period. The formation of biochemical and physical reactions during ripening plays an important role in the texture and taste of matured cheese [19]. The cholesterol ratio of cheese samples increased until the 45th day, decreased by 60th and 90th day. The average amount of cholesterol in cheese samples was found as 85.77 mg/100g. The value found is higher than the value found in Kars Gravyer Cheese (54.23 mg/100) by Karagözlü et al. [20] between the values (44.6–147.769 mg/100) found in some local Turkish by Dönmez et al. [21] and close to values (82.52 mg /100 g) in Gouda cheese by Ho-Jung et al. [8].

As a result of the literature review, no research was found related to the determination of fatty acids profile in the production and storage stages of Kars Gravyer Cheese. For this reason, the results obtained from this research will be interpreted taking into consideration the studies conducted in other cheese varieties. Table 4 and 5 show that the fatty acid ratios of the Kars Gravyer Cheese samples changed during the maturation period from the production stage. This may be due to biochemical processes occurring in different maturity periods of the cheeses. Double carbon saturated and unsaturated 16 fatty acids were identified in Kars Gravyer Cheese samples. According to the results of the analysis, the highest fatty acids in the cheese samples were palmitic, oleic, stearic and myristic fatty acids. Ratios of butyric (C4: 0), caproic (C6:0), caprylic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), pentadecanoic (C15:0), palmitic (C16:0), heptadecanoic (C17:0), stearic (C18:0), myristoleic acid (C14:1), palmitoleic (C16:1), oleic (C18:1), elaidic (C18:1 (trans 9), linoleic (C18: 2) and 11 –eicosenoic (C20: 1) acid identified in cheese samples ranged between 2.56–2.74 mg/100g, 1.46–2.04 mg/ 100g, 0.74–1.38 mg/100g, 2.17–3.18 mg/100g, 2.67–3.72 mg/100g, 11.11–12.57 mg/100g, 1.45–1.72 mg/100g, 27.73–29.81 mg/100g, 0.74–0.97 mg/100g, 13.24–15.16 mg/100g, 0.66–0.92 mg/100g, 1.64–1.92mg/100g, 20.19–23.12 mg 100g, 4.20–6.27 mg/100g, 0.33–0.46 mg/ 100g and 1.13–1.43 mg/100g respectively.

Changes in the total free fatty acids C4, C6, C10, C14, C16, C18, C14:1, C16:1, C18:1n9T and C18:1 n9C values of all cheese samples during the ripening period were statistically significant ($P < 0.001$, $P < 0.01$, $P < 0.05$) and the changes in C8, C12, C17, C18:2 and C20:1n9 values were statistically insignificant ($P > 0.05$).

Abd El-Salam [22] reported that milk varieties, maturation temperature, salt concentration, milk lipase, starter bacteria and other microbial lipases were also effective on the formation of free fatty acids in cheese such as Feta and Teleme. Free fatty acids are primarily formed by the enzymatic breakdown of glycerides in dairy products [23]. Free fatty acids, as they directly contribute to the flavor of the cheese, also play a role in many types of reactions leading to the formation of methyl ketones, secondary alcohols, aliphatic and aromatic esters [24]. The free volatile fatty acids found in cheeses are closely related to flavor and aroma, and acetic, butyric, caproic, caprylic and capric acids are the most important free fatty acids affecting the cheese flavor [24].

In Kars Gravyer Cheese samples, the amount of volatile fatty acids (C4: 0-C14: 0) increased up to 25th day ($P < 0.01$) and decreased from 45th day to 90th day. While levels of free fatty acids (C16: 0-C18: 2) generally decrease at day 25, they have begun to increase again until the end of the ripening period. Kara et al. [25] stated that the proportion of fatty acids in tulum cheese increased until the 30th day and then decreased until the 90th day. In the studies carried out by different researchers [26–28], the level of volatile fatty acids has been reported to rise during maturation. Unlike other studies, free fatty acids increased up to the 25th day and then decreased periodically (45–90 days). The reason for the decline in free fatty acids between 45 and 90 days is that some of the free fatty acids that occur at the

end of maturation are converted into β -oxidation and methyl ketones, carbonyl compounds and other decomposition products [29].

Short and mid-chain saturated free fatty acids such as butyric, caproic, caprylic and capric acid are often the result of lipolysis of triglycerides by molds. However, in some cases, fatty acids containing up to six carbon atoms can be formed by the reduction of lactose and amino acids or the oxidation of ketones, aldehydes, and esters ([30]. Short and medium chain fatty acids have a low sensory perception threshold and have a more significant effect on the flavor development of cheese than long chain fatty acids.

In this study, the average values of butyric, caproic, caprylic and capric acid during 90 days maturation period in Kars Gravyer cheese were found as 2.56–2.74 mg/100g, 1.72–2.04 mg/100g, 1.07–1.38 mg/100g and 2.55–3.18 mg/100g respectively. The values obtained are higher than the values found by Türkoğlu, [27], in braided cheese and by Atasoy et al. [26], in Urfa cheese and lower than the values found in Van Otlu Cheese by Ocak et al. [31], and the values found in 11 different cheese varieties by Hayaloğlu et al. [32], Palmitic, oleic, myristic and stearic acid formed in gravyer cheese during maturation accounted for 74.29 % of the total free fatty acids content. The most abundant fatty acids in fresh and ripe gravyer cheeses are palmitic acid (C16:0). This ratio varied between 27.73–29.81 mg/100g. Other acids following this fatty acid are oleic (C18:1) (20.19–23.12 mg/100g) stearic acid (C18:0) (13.24–15.16) and myristic acid (C14:0) (11.11–12.57) respectively. This may be due to the presence of large amounts of palmitic, oleic, stearic and myristic fatty acids in milk fat [33]. The values identified in gravyer cheese are higher than the values obtained by Atasoy et al. [26], in Urfa cheese (myristic acid 6.37–12.40 mg/100g, palmitic acid 18.0–26.9 mg/100g and oleic acid 12.7–19.00 mg/100g) and lower than the values found in 11 different cheese varieties (myristic acid 6.2–139.7 mg/100g, palmitic acid 19.9–356.7 mg/100g and 17.6–386.3 mg/100g) by Hayaloğlu et al. [32], Mallatou et al. [34], reported that although palmitic, stearic and oleic fatty acids form dominant fatty acids in feta cheese, these fatty acids were not as effective as short-chain fatty acids on cheese flavor. Lauric acid (C12:0) is the predominant fatty acid (2.67–3.72 mg/100g) among short and medium-chain fatty acids. Aminifar et al. [35], Marrone et al. [36], and Ocak, et al. [31]. Şengül et al. [3], and Arslaner et al. [28], reported that palmitic, myristic, stearic and oleic fatty acids had the highest proportion among the fatty acids in Lighvan cheese, in Pecorino Carmastiano cheese, in fresh and ripe Herbed cheeses, in Karın kaymağı cheese samples and in Tulum cheese respectively. In addition, Ocak et al. [31], stated that lauric acid (C12:0) was the predominant fatty acid among short and medium-chain fatty acids. The amounts of oleic and especially linoleic acid, which are very important in terms of nutrition physiology and which cause certain dermatological diseases and increase in the water permeability of cells in their deficiency or absence in the diet are determined as 20.19–23.12 mg /100g and 0.33–0.46 mg/ 100g respectively.

Elaidic acid (C18:1) acid level increased up to 60 days during maturation but decreased for 90 days. The contents of linoleic acid (C18: 2) (0.33–0.46 mg/100g) and cis-11-eicosenoic acid (C20:1) (1.13–1.43 mg/100g) of fresh and ripe Gravyer cheeses were found to vary within a narrow range. Cheese fat contains saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids. Milk fat generally contains approximately 66% saturated (SFA) (57.4% palmitic, 21.6% myristic and 17.6% stearic), 30% monounsaturated (MUFA) and 4% polyunsaturated fatty acids (PUFA) (López-Expósito, Amigo, & Recio, 2012). Of the fatty acids identified in the cheese samples, 68.22% were saturated fatty acids and 31.77% were unsaturated fatty acids. Dönmez et al. [21], determined saturated fatty acid ratio as 60.80–76.57%. Short, medium and long chain fatty acids were determined as 4.84–6.15%, 15.95–19.47% and 71.43–76.57% in Kars

Gravyer Cheese samples, respectively. According to values determined in Gravyer Cheese: Atasoy et al. [26], in Urfa cheese (7–8%, 20–23% and 70–72%) and Sert et al. [38], found in tulum cheese (15.08–22.51%, 39.13–42.62% and 30.92–38.56%), Turkoglu [27], found in braided cheese (medium and long chain fatty acids 24–27% and 63–72%) that short chain (SCSFA) and medium-chain (MCSFA) fatty acids were low and low-chain fatty acids (LCSFA) were high in concentration. In cheese samples, the proportions of monounsaturated fatty acid (MUFA) and polyunsaturated fatty acid (PUFA) were found to be 28.38–32.37% and 1.59–1.84%, respectively Dönmez et al. [21], found in some traditional Turkish cheeses, that MUFA was 21.42–34.05% and PUFA 1.47–3.59% and Kınık et al. [39]. In 29 different hard and soft cheese varieties, MUFA was determined as 24.14–27.63 and PUFA as 0.72–1.58%. The values found in Gravyer cheese were higher than found by Kınık, et al. [39], approximately around the same MUFA value range found by Dönmez et al. [21], and lower than the PUFA values of the same study.

The Atherogenicity (AI) index, desired fatty acids (DFA) and ASFA / SFA ratios were determined as 2.57–3.04, 43.46–48.05 and 0.43–0.49 in Kars Gravyer Cheese samples, respectively. The values found were higher than the AI value determined in traditional Serbian white cheese (1.89–3.06) by Barac et al. [5], in Serbian traditional white cheeses, higher than the lower limit of DFA (34.45–46.34), lower than the upper limit, and higher than USFA/SFA (0.30–0.51).

Conclusion

This study was the first to examine the changes in free fatty acids and cholesterol levels and examine the effect of ripening days on the change of fatty acid composition and cholesterol level during maturation starting from production. In the 90 day storage period of Kars Gravyer Cheese, palmitic, oleic, myristic and stearic acid constituted 74.29% of the total free fatty acids content and while the most abundant saturated fatty acids were palmitic and stearic acid, oleic acid was the most abundant unsaturated fatty acid. The cholesterol content of cheese samples ranged from 45.70 to 55.80 mg/100g during 90 days of maturation. In this study, the distribution of saturated and unsaturated fatty acids in milk fat, which is very important in terms of human nutrition, was determined in Kars Gravyer Cheese. In cheese samples, 10 saturated fatty acids and 6 unsaturated fatty acids were determined and medium and long-chain fatty acid ratios were found to be higher than short chain fatty acids. Conversion of triglycerides into free fatty acids by microorganisms and natural milk lipase plays an important role in the development of different aroma substances in ripe cheeses. Especially short and medium chain free fatty acids are used as precursors in the formation of aromatic products such as ethyl ketones, esters and thioesters [31, 40]. It can be said that Kars Gravyer Cheese is a very aromatic cheese because it contains short and medium chain fatty acids which have an important effect on the flavor and aroma of milk and dairy products. Having said that, this research is also important in terms of shedding light on the research to be carried out in the future.

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Identification of beeswax and its falsification by the method of infrared spectroscopy

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Abstract

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Introduction. The purpose of the research was to determine the characteristics of the infrared spectra of reflection and absorption of beeswax, as well as wax with the content of impurities in it, in particular paraffin and ceresin.

Materials and methods. Natural beeswax, paraffin, ceresin, as well as their mixtures were investigated by infrared spectroscopy of reflection and absorption using Infrapid-61, Luminar 5030 and SPECORD M-80 spectrometers.

Results and discussion. Infrared reflection spectra from smooth surfaces of samples (paraffin, ceresin, wax, a mixture of beeswax and ceresin, a mixture of wax paraffin and ceresin, a mixture of wax and paraffin) have a similar structure. There are two clearly expressed maxima at wavelengths of 1510 and 1581 nm. The ratio $R_w(1581)/R_w(1510)$ varies from 1.115 to 1.265. The smallest value corresponds to natural beeswax, and the maximum value is ceresin. After shredding the sample, the infrared spectral diffuse reflections did not undergo significant changes, the most intense spectral maxima did not change its position, but the redistribution of spectral lines by intensity was happened out. There were pronounced differences in the region from 1723 to 2400 nm. The coefficient α for the reflection spectra from the smooth surface was ~ 1.2 , and for the reflection spectra from the crushed samples ~ 1.1 . The reflection spectra in the region from 1100 to 1350 nm have a clear maximum at a wavelength of 1212.5 nm.

IR reflection spectra allowed us to clarify the difference between the natural beeswax and ceresin through the ratio of reflection features at 1510 and 1581 nm: the maximal ratio corresponded to the former, while the smallest one to the latter. The different proportion of bands corresponding to CH_2 and CH_3 stretching vibrations suggested that hydrocarbon chains of wax molecules are longer than those of paraffin and ceresin studied. It was found that hydrocarbon contaminants in the bee wax are associated with narrowing of the $\text{C}=\text{O}$ band at $\sim 1736 \text{ cm}^{-1}$.

Conclusions. The detected spectral laws will enable the identification of natural beeswax and detect its counterfeit.

Introduction

Bee wax is widely used in many branches of the national economy [1, 2, 29], as well as in metallurgical, electrical, chemical, pharmaceutical [3-5], food industry, in particular in the production of cheese and sweets, as well as the coverage of fruits and vegetables in order to increase their shelf life [6, 30]. However, most of the wax is returned to beekeeping for the industrial production of wax.

Waxes with impurities are called counterfeit [7-10]. It poses a serious threat to the beekeeping industry. The falsification of beeswax causes economic and image losses of the industry, worsens the productivity and quality of honey, and also significantly reduces the welfare of honey bees. The most common impurities that are added to beeswax are paraffin, ceresin, microcrystal wax, fat, stearic acid, clay, sand, hard fat, chalk, gypsum.

The high cost of beeswax compared with other waxy products (paraffin, ceresin), as well as the fact that it is quite difficult to distinguish the impurities from natural wax by external signs, making beeswax attractive for falsification [11].

According to the current requirements of quality, the industry is allowed to produce wax with insignificant content of paraffin and ceresin, but in order to improve the quality of beekeeping products and to avoid further complications, it is desirable to avoid the presence of these unnatural impurities.

Currently, there are a number of classic traditional methods for verifying the authenticity of beeswax [11] and controlling its quality: organoleptic, chemical research methods, high temperature gas chromatography and other diagnostic methods. However, such studies are long-term in time and usually lead to the destruction of researched sample.

It should be noted that the existing methods of control – organoleptic, chemical, physical, – although reliable, but morally and technically obsolete [11, 12], and do not correspond to the current level of quality control of products of beekeeping [13, 14]. An urgent need for modern methods of quality control [15, 16] is due to the fact that fake beeswax is a direct threat to the existence of honey bees, and can negatively affect the quality of all products of beekeeping.

The purpose of the research was to determine the characteristics of the infrared spectra of reflection and absorption of beeswax, as well as wax with the content of impurities in it, in particular paraffin and ceresin.

Research of wax raw materials by obtaining IR reflection spectra does not foresee the use of reagents and allows identification of beeswax, as well as draw conclusions about its falsification. This method is fast, direct and non-destructive.

These benefits of the method allow you to save time and money, and also allow you to explore more samples per unit time.

The use of high-quality natural beeswax is a necessary condition for obtaining organic (natural) bee products [17-20].

Materials and methods

Materials

Wax was obtained on the apiary of the Kyiv-Svyatoshinsky district of Kyiv region 20 years ago by melting old honeycomb in a steam kettle. The wax was stored in a dark place at room temperature in the form of blocks of cylindrical shape with a diameter of 30

centimeters and a height of 10 centimeters, in a closed package (sack) of dense fabric. Paraffin used in medicine was used for conducting experiments.

Cerezin was taken at the enterprise of the wax processing industry, which got there in the form of counterfeit raw materials. In the process of chemical analysis, it was found that the test sample is ceresin, and has nothing to do with beeswax. According to external signs (color, plasticity, fragility, structure of breakage, etc.) the sample was identical to natural beeswax, which made it impossible to identify it without the use of physico-chemical methods of analysis.

Before the beginning of the research, the samples were melted to a liquid state at a minimum melting point (~ 65 degrees Celsius). Subsequently, the liquid was poured into a special form, where it was cooled to room temperature, and hardened. Thus, three samples were obtained: natural beeswax, paraffin and ceresin. Similar samples were obtained with different concentrations of paraffin and ceresin in natural beeswax. The relative homogeneity of the samples was obtained by mixing the components in the melting process, their small mass and, as a result, a fairly small hardening time (about a few minutes). The above factors made it possible to avoid explicit stratification of the sample, due to a slightly different density of its components. The diameter of the cylindrical specimens was 5 cm and their height was 5 mm, the dimensions correspond to the cuvette of the Infracid-61 infrared diffraction reflector. During solidification a smooth (glossy) surface was formed.

Separately, to increase the accuracy of the experiment, new samples were prepared in analogy to the previous one, with only one difference: natural beeswax was taken from the swarm family. As is known, during the rebuilding of honeycombs, bees take wax from the very beeswax, adding only about 20 percent of their wax to newly built honeycombs. That is, if the beeswax, contaminated by impurities, enters the apiary, then after the melting process these impurities will be present in wax. This will greatly complicate the conduct of the experiment [21].

To obtain spectra of diffuse reflection in the near infrared region, each sample was mechanically shredded with the device that is a set of metal equidistant knives of the same size.

For IR absorption spectroscopy, the samples were mixed with the KCl powder and pressed as pellets. The reference samples represented pure wax, cerezine and paraffin material. In order to study the effect of wax contamination by cerezine or paraffin, certain amount of wax was mixed with one or both latter materials in different proportions. The typical spectra here are presented for samples with approximately equal proportions of the components in the mix.

Research methods

The reflection spectra from a smooth surface and shredded samples were researched by using the Infracid-61 spectrometer in the near infrared range from 1330 to 2370 nm. The spectrometer initially recorded the reflectance spectrum from reference I_0 (component part of the instrument), then a reflection spectrum from the researched sample I was obtained. The spectra are represented as the reflectivity of R in relative units (the ratio of the intensities $I/I_0 = R$), depending on the wavelength in nm.

The Luminar 5030 spectrometer recorded reflection spectra from the unprepared surface of the samples. Each sample was scanned 150 times in 1 nm increments. By averaging the results, reflectance spectra were obtained for each object of the research. The process of scanning one sample lasted about 7 seconds.

IR absorption was studied using a dual-beam SPECORD M-80 spectrophotometer in the 4000 to 800 cm^{-1} range. As all the samples demonstrated similar fingerprints near 3000 cm^{-1} corresponding to CH_3 and CH_2 stretching, the spectra below are given only in the region of 1900-600 cm^{-1} , where characteristic IR vibrations of the polymers are displayed [22-28].

Results and discussion

NIR reflection research

Infrared reflection spectra from smooth surfaces of several samples (P – paraffin, C – Ceresin, W – Wax, WC – a mixture of beeswax and ceresin, WCP – a mixture of wax paraffin and ceresin, WP – a mixture of wax and paraffin) are shown in Figure 1. All the spectra have a similar structure. There are two clearly expressed maxima of 1509 and 1581 nm (features c and e in Figure 1) and more than four minima, in particular at 1415, 1533, 1725, and 2254 nm (features b, d, f, g). The highest intensity in the reflection spectrum corresponds to the wavelength of 1581 nm.

Analyzing the ratio of the maxima of the corresponding spectra for wavelengths of 1510 and 1581 nm (Table 1), we can conclude that the parameter α , which is equal to the ratio $R(1581)/R(1510)$, varies from 1.115 to 1.265. The smallest value

$$\alpha = \frac{R_{W(1581)}}{R_{W(1510)}} = 1.115 \text{ corresponds to natural beeswax, and the maximum value}$$

corresponds to ceresin $\alpha = \frac{R_{W(1581)}}{R_{W(1510)}} = 1.265$. Among the spectral features it is

worthwhile to mention the characteristic intervals between extremums (Figure 1, Table 2): BC = 94, CE = 72, EF = 145 nm.

After shredding the sample the infrared spectrum of diffuse reflection did not undergo significant changes, the most intense spectral maxima did not change its position (Figure 4), but the redistribution of spectral lines by intensity was carried out. There were pronounced differences in the region from 1723 to 2400 nm (Figure 4), in contrast to the spectra obtained from the smooth surface of the sample (Figure 1).

Analyzing the positions of the spectral line maxima (Figure 1) at wavelengths of 1581 and 1510 nm (Table 1), it can be noted that they are located in the following sequence $R_P > R_{WP} > R_{WC} > R_{WCP} > R_C > R_W$.

The coefficient α for the reflection spectra from the flat surface is ~ 1.2 , and for reflection spectra from shredded samples is ~ 1.1 (Table 1 and 2).

Figure 5 presents the IR reflection spectra in the spectral range from 1100 to 1350 nm, obtained with the device Luminar 5030. The horizontal axis deferred wavelength in nanometers, while the vertical axis optical density is $\lg 1/R$, where R – reflecting the ability of the body.

Differences in intensity of the spectral characteristics of the researched samples at a wavelength of 1212.5 nm allow to make conclusions concerning presence of impurities (wax and ceresin) in the researched samples.

Spectral maxima at the specified wavelength are located in the following sequence $R_P > R_W > R_{WCP} > R_{WC} > R_{WP} > R_C$.

Table 1
Ratio of the intensities of the spectral maxima
for 1510 and 1581 nm.
Smooth surface

Sample	R ₁₅₁₀	R ₁₅₈₁	R ₁₅₈₁ /R ₁₅₁₀
W	0.309	0.357	1.155
P	0.318	0.397	1.248
C	0.310	0.392	1.265
WP	0.375	0.448	1.195
WC	0.328	0.394	1.201
WCP	0.318	0.394	1.239

Table 2
Ratio of the intensity of the spectral maxima
for 1510 and 1581 nm.
Shredded sample

Sample	R ₁₅₁₀	R ₁₅₈₁	R ₁₅₈₁ /R ₁₅₁₀
W	0.879	0.932	1.06
P	0.743	0.827	1.11
C	0.727	0.806	1.12
WP	0.792	0.857	1.08
WC	0.757	0.824	1.09
WCP	0.799	0.874	1.09

Table 3
Characteristic intervals between spectral extremums (Figure 1)

Extremum	Coordinate	Segment	Length of the segment, nm
A	1397	AB	18
B	1415	BC	94
C	1510	CD	24
D	1533	DE	48
E	1581	EF	145
F	1726	FG	528
G	2254	GH	45
H	2299	HI	57
I	2356		

The W_{original} spectral line (Figure 5) corresponds to a rough (not molded) sample of beeswax obtained on an apiary 20 years ago. Spectral line W is obtained from a melted sample. The indicated differences in the infrared reflection spectra can be used in obtaining information concerning the history of the production of wax raw materials.

In the article [1] a relatively new direct method for the investigation of wax was proposed, without the use of chemical reagents. The method involves the use of IR spectroscopy in the range from 4000 to 650 cm⁻¹. It allows you to identify beeswax and detect fake (impurities). In the described method, the absorption coefficient was recorded, namely the ratio: $I_{1739\text{ cm}^{-1}}/I_{2852\text{ cm}^{-1}}$, $I_{1714\text{ cm}^{-1}}/I_{2852\text{ cm}^{-1}}$, $I_{1739\text{ cm}^{-1}}/I_{1714\text{ cm}^{-1}}$. The results of the studies were confirmed by high temperature gas chromatography. The difference between this work and the previous one is that the absorption and reflection spectroscopy was used. The registration of absorption spectra took place in the spectral range from 1900 to 600 cm⁻¹, and the reflectance spectra were recorded in the range from 1500 to 2400 nm.

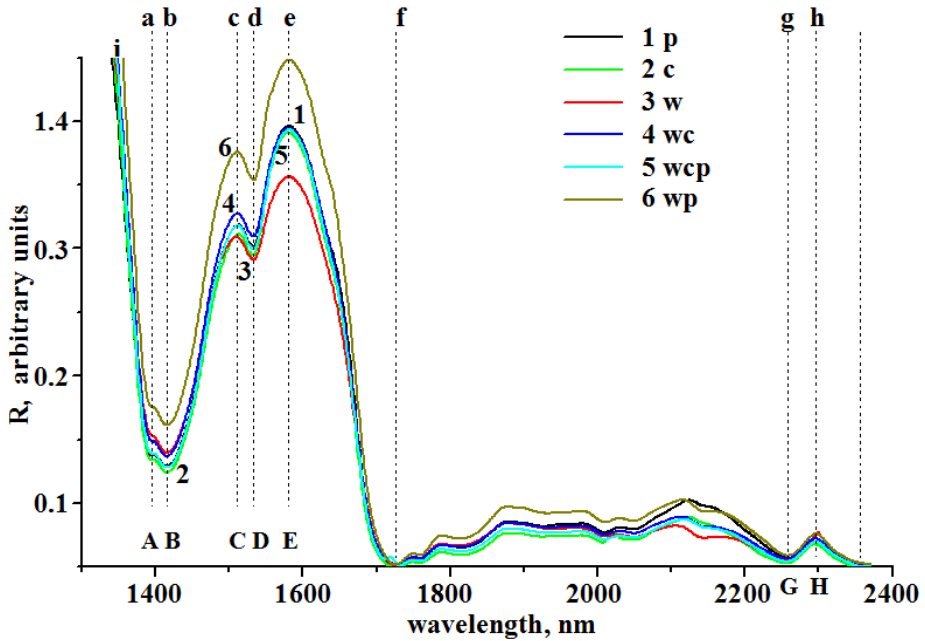


Figure 1. IR reflection spectra. Smooth (glossy) surface of the samples: p – paraffin, c – ceresin, w – natural beeswax, wc – a mixture of wax and ceresin, wcp – a mixture of bee wax, ceresin and paraffin wax, wp – a mixture of wax and paraffin

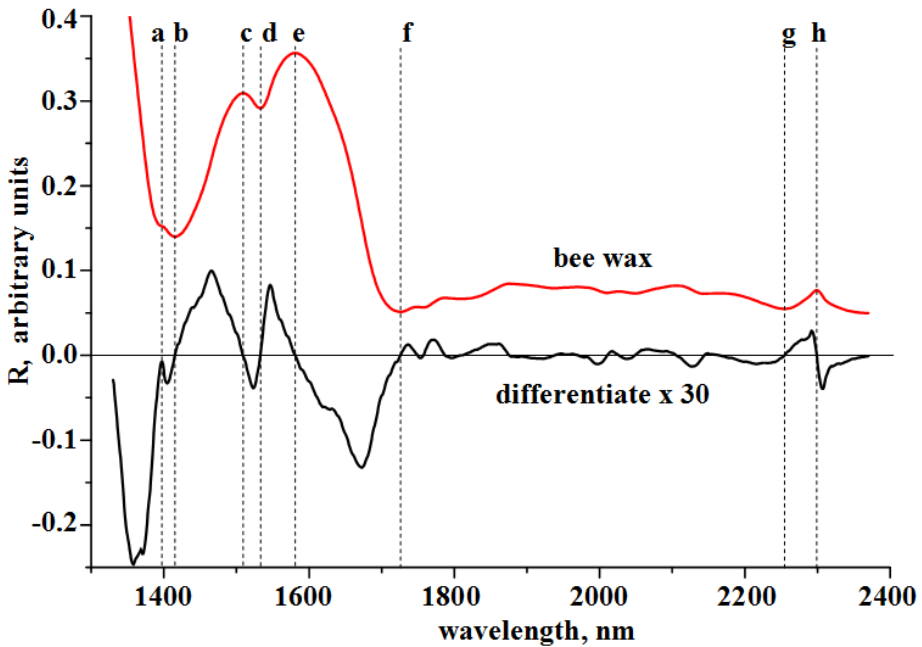


Figure 2. IR reflection spectrum of natural beeswax and its first derivative

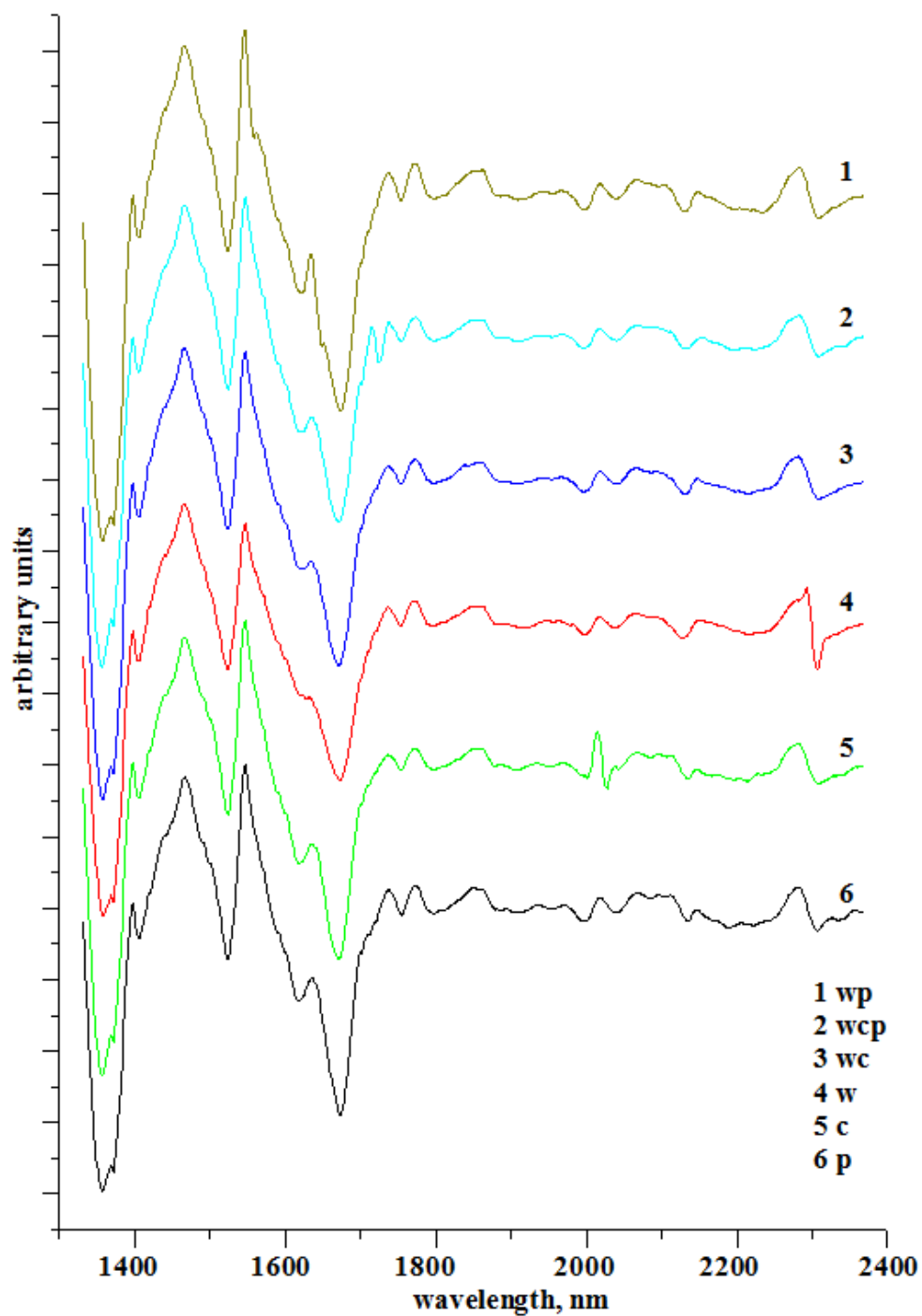


Figure 3. First derivatives of IR reflection spectra from a smooth surface of samples

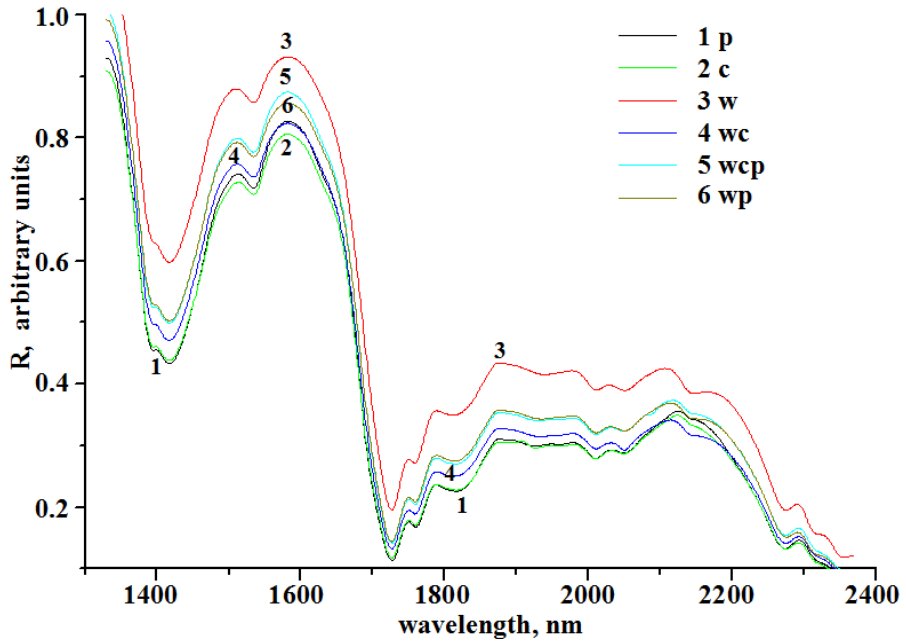


Figure 4. IR spectrum of diffuse reflection of shredded samples

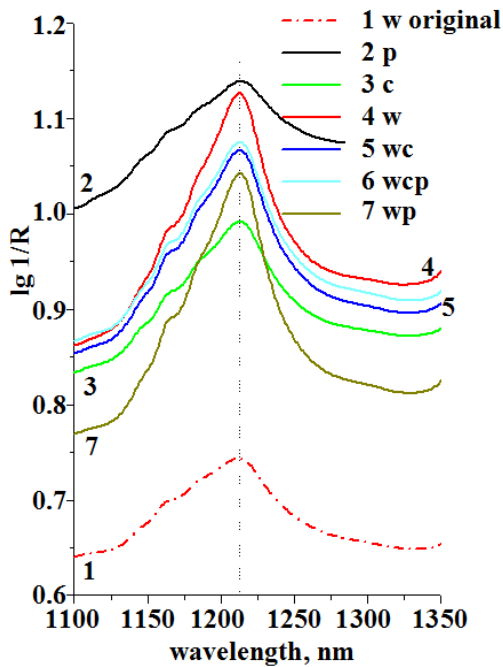


Figure 5. IR reflection spectra of waxy substances

Wax is considered to be a fairly stable compound, with virtually unlimited shelf life, provided that proper storage conditions are met. At the same time, in the long-term storage, especially in non-leakproof containers at high temperatures, the surface of the sample undergoes certain changes in the physical and chemical parameters, which visually manifests itself in the change of color, and as a consequence in the features of the reflection spectra, and so on. This fact needs to be taken into account in optical studies, since the information received with the help of infrared reflection spectroscopy essentially depends on the state of the surface of the sample.

To some inconvenience of the use of IR reflection spectroscopy one can attribute the fact that the spectra have a similar structure, and it is difficult to distinguish them visually from each other (Figure 1, 4). The proposed research methodology needs improvement in the detection of impurities of low concentration (several percent and less). Interpretation of the results may be complicated if there is a large number of impurities of different chemical nature. In studies, it is necessary to take into account the state of the surface of the sample, and if necessary, to shred (break) the sample, or to melt it. In a case of presence of a large amount of water in beeswax (more than 20%) the use of infrared spectroscopy is ineffective.

IR absorption research

Typical spectra of IR absorption of the neat components are shown in Figure 6.

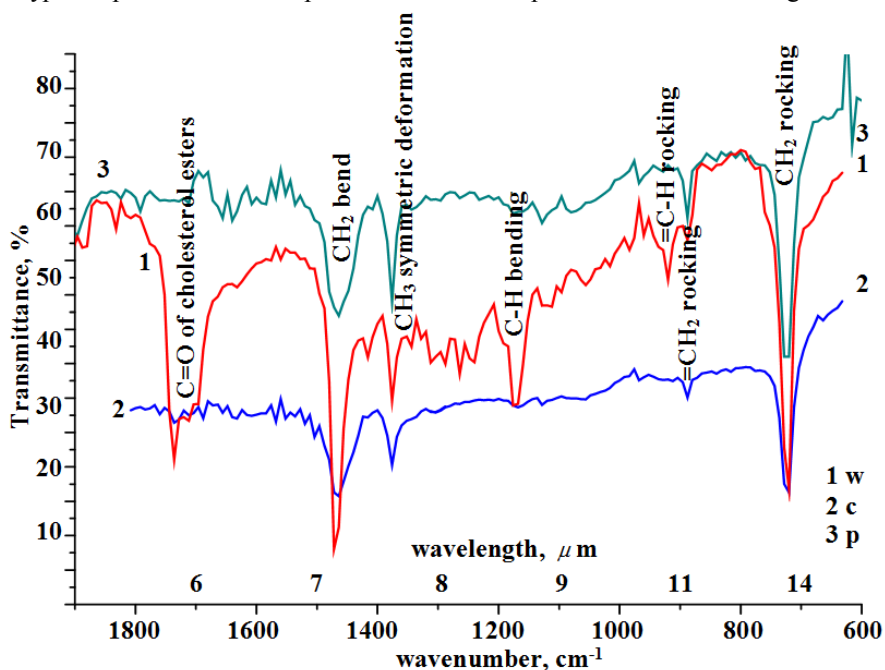


Figure 6. IR spectra of (1) wax, (2) ceresin and (3) paraffin reference samples

All the samples demonstrate similar bands, i.e., at 1470 cm^{-1} corresponding to CH_2 bending, 1376 cm^{-1} corresponding to CH_3 symmetric deformation, 1170 cm^{-1} corresponding to C-H bending, 888 and 720 cm^{-1} corresponding to CH_2 rocking. The above features are typical for hydrocarbon chains and reflect the fact that the compounds have similar chain

fragments. However, one can distinguish different proportion of the above band intensities. Particularly, the different proportion of CH₂ and CH₃ bands suggests that hydrocarbon chains of wax molecules are longer than those of paraffin and cerezine studied. One more difference is that the spectrum of wax is more reach than those of paraffin and cerezine. Particularly, the wax samples demonstrate a strong C=O vibration at ~1736 cm⁻¹ corresponding to cholesterol esters. This band is a characteristic feature which allows one to identify wax among other hydrocarbon compounds.

The mixtures of wax with other compounds demonstrate CH, CH₂ and CH₃ bending and rocking vibrations in IR spectra characteristic for all hydrocarbons used (Figure7).

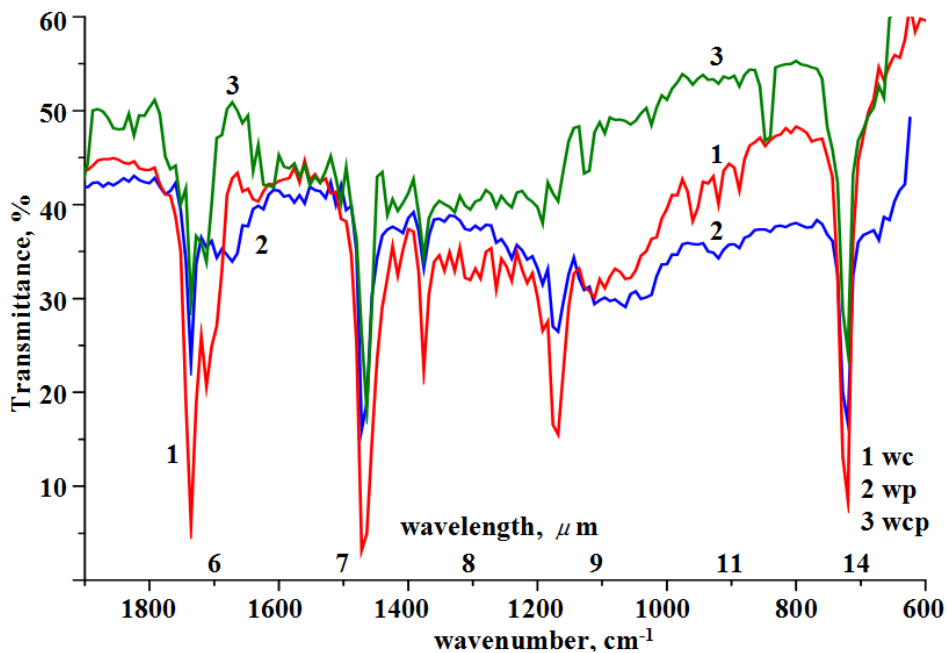


Figure 7. IR spectra of mixtures of (1) wax plus ceresin, (2) wax plus paraffin and

The spectra are also enriched with the strong C=O vibration at ~1736 cm⁻¹ indicative of the presence of wax. However, in the mix samples, this band has a more complex structure compared to the neat wax. In fact, the C=O band is splitting in the mixtures, with a strong component at ~1736 cm⁻¹ for all the samples accompanied by a smaller red-shifted one. Position of the latter component is dependent on the mixture composition: for the wax-cerezine mixture it is at 1712 cm⁻¹, for the wax-paraffin mixture it is at 1672 cm⁻¹, and for the wax-cerezine-paraffin mixture it is at 1712 cm⁻¹ again. The splitting and shift of the C=O band is related to the different environment for the carbonyl group in the mix samples, when part of these groups remains in the native wax environment whereas the other in the foreign paraffin or ceresin environment, respectively. In fact, the spectrum of the neat wax (Figure 6) also contains the component at 1712 cm⁻¹, however, this component is less resolved due to broadening of the C=O band itself, suggesting more polar environment for

the carbonyl group in the wax. The different broadening of the C=O band is shown in Table 4 and the factor can be used for identification of the contaminant in the bee wax itself.

Table 4
Full width at half maximum (FWHM) of the C=O band in the neat wax and mixed samples

Composition	W	WC	WP	WCP
FWHM (cm ⁻¹)	62	45	20	43

Thus, our results evidence that hydrocarbon contaminants in the bee wax are associated with narrowing of the C=O band at ~1736 cm⁻¹. This spectroscopic feature can be used for further quantitative analysis of the purity of the bee wax itself.

Conclusions

1. Infrared reflection spectra (in the range of wavelengths 1330–2370 nm) from smooth surfaces of samples (paraffin, ceresin, wax, a mixture of beeswax and ceresin, a mixture of wax paraffin and ceresin, a mixture of wax and paraffin) have a similar structure, but there are two clearly expressed maxima of different intensity at wavelengths of 1510 and 1581 nm.
2. The ratio of the intensity of the reflection spectra at characteristic wavelengths $\alpha = R_w(1581)/R_w(1510)$ varies from 1.115 (natural bee wax) to 1.265 (ceresin).
3. The maximum intensity of optical density is observed at a wavelength of 1212.5 nm, which can be used to identify the wax and allow conclusions to be made regarding the aging of the sample.
4. Infrared spectra of diffuse reflection of shredded samples will not undergo significant changes in comparison with spectra from a smooth surface. The most intense spectral maxima do not change their position, but there is a redistribution of spectral lines by intensity.
5. The different proportion of CH₂ and CH₃ bands suggests that hydrocarbon chains of wax molecules are longer than those of paraffin and cerezine studied. One more difference is that the spectrum of wax is more reach than those of paraffin and cerezine. Particularly, the wax samples demonstrate a strong C=O vibration at ~1736 cm⁻¹ corresponding to cholesterol esters. This band is a characteristic feature which allows one to identify wax among other hydrocarbon compounds.

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Antimicrobial properties of model drugs in the systemic concept of health

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Abstract

Keywords:

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Microorganism
Resistance
E. coli
Antimicrobial
Health

Introduction. We analyzed the antimicrobial efficacy of the investigated preparations of the KTIOL-BF series on standard culture of microorganisms: *S. aureus*, *Escherichia coli*, *P. aeruginosa* and *S. saprophyticus*.

Materials and methods. The model preparations of the KTIOL-BF series (biofunctional) are studied. The preparations are based on vegetable and animal extracts containing iodine solution or do not contain it. As controls, preparations of povidone iodine and chlorophyll are used. The antimicrobial properties of the samples of the preparations were determined by the modified diffusion method ("wall" method) for increasing the upper range of evaluation.

Results and discussion. The scientific basis of this study is the systematic concept of health, developed on the basis of the KTIOL-I ecological-technological system and the physiologically functional system KTIOL-II. The preparation on the basis of herbal extract provided the initial good antimicrobial effect on all microorganisms studied. Introduction to the preparation based on extracts of plants and on the basis of plant and animal extracts with solution of nanosized particles of colloidal silver up to 35 wt. % slightly reduced the antimicrobial effect of the samples relative to *S. aureus* and *S. saprophyticus*. The sample on the basis of plant and animal extracts showed a good antimicrobial effect on microorganisms *S. Saprophyticus*, *E. coli*, *P. aeruginosa*. Two samples showed a good antimicrobial effect on all studied microorganisms.

Model samples of the preparation on the basis of two-phase plant modified enzymes produced a very good integral antimicrobial effect on all microorganisms studied. Of these, two samples based on extracts of plants and on the basis of plant and animal extracts showed high antimicrobial effects on the *E. coli* strain (30 mm growth retardation diameter).

The possibility of high antimicrobial action on *E. coli* strain (30 mm diameter growth delay) has been confirmed. This is due to the complex action of these two samples on the study of gram-positive and gram-negative strains of microorganisms.

Conclusions. The possibility of high antimicrobial activity of samples on the basis of two-phase plant extract and on the basis of plant extract and iodine solution on strain *Escherichia coli* was revealed and confirmed. The same specimens showed high and good antimicrobial properties, both in other strains, and in an integral manner.

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Introduction

Modern livelihoods of Man contributes to the accelerated proliferation of pathogenic and the emergence of resistant microflora, which interacts with human saprophytic microbes and can affect our physical health. Saprophytic microbes are trillions of microbes living on the surface and inside our body.

It is also important for scientists to find evidence that intestinal bacteria use tiny strips of a genetic code called "miRNA" to change the way DNA acts in nerve cells [1].

In prophylaxis and treatment of infectious diseases are crucial the using of functional drugs for general and local therapy and/or the individual application of the systemic concept of health [2].

Kovan M.M. in the review [3] analyzed the possibility of using plant products as antimicrobial agents. The use of and search for drugs and dietary supplements derived from plants have accelerated in recent years. Ethnopharmacologists, botanists, microbiologists, and natural-products chemists are combing the Earth for phytochemicals and "leads" which could be developed for treatment of infectious diseases. While 25 to 50% of current pharmaceuticals are derived from plants, none are used as antimicrobials. Traditional healers have long used plants to prevent or cure infectious conditions; Plants are rich in a wide variety of secondary metabolites, such as tannins, terpenoids, alkaloids, and flavonoids, which have been found in vitro to have antimicrobial properties. This review attempts to summarize the current status of botanical screening efforts, as well as in vivo studies of their effectiveness and toxicity. The structure and antimicrobial properties of phytochemicals are also addressed. Since many of these compounds are currently available as unregulated botanical preparations and their use by the public is increasing rapidly, clinicians need to consider the consequences of patients self-medicating with these preparations.

In the author's opinion, it would be beneficial to standardize in vitro extraction and testing methods in order to more systematically find and facilitate the interpretation of results.

Gerontologists also recommend starting prevention as early as possible [4–6].

Now we can observe rasing of the microflora and hospital strains resistance to antibiotics and antiseptics, and as results - increasing in the frequency of secondary and postoperative infections [7].

The aim of the study. To reveal the antimicrobial properties of the different investigated specimens KTIOL-BF series, obtained from the systemic concept of health (KTIOL®) [3].

Systemic concept of health (The systems KTIOL®). The system KTIOL-I (Comprehensive Technologies, Engineering, Equipment, Lines) was initially aimed at the synthesis of lipid-containing products of special purpose. The main principles of the system KTIOL-I: providing the structure of the product (preparation) at the micro and nano level; ecological and economic efficiency; a systematic approach to the methodology of producing safe food, pharmaceutical and cosmetic products and drugs'

The system of KIIOL-II (Integrated Therapy of Individual Health Improvement) was initiated from the analysis of indicators of quality and safety of water, food products, dietary supplements and preparations, environmental and endoecological aspects of personal health. The KIIOL-II system includes: hygiene of thoughts (positive thinking and positive mood); sleep hygiene (recovery, rehabilitation, treatment, rehabilitation); prevention (ophthalmologic, dental, endoecological, herrolontal); water is high quality and safe; nutrition organic and health-care; breathing health-curative; Individual systemic

exercise (walking, massage, swimming, tennis, Scandinavian walking, etc.); meditators and self-adjusting; individual know-how [2, 5, 8].

Means based on vegetable, ethereal oil and other sources. In recent data, we found information about the influence of the molecular structure of derivatives of 4-thiazolidine (about 70 compounds) on their antimicrobial activity was investigated by the QSAR method. Microorganisms were used as reference cultures: *Candida albicans*, *S. Citrobacter freundii*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* MSSA [9].

The influence of the evolution of the heterocyclic system on the antimicrobial properties of derivatives of 4-thiazolidines was demonstrated. An important role of electrostatic characteristics of their molecular structure was also shown. The compounds with the highest predictive value of antimicrobial activity against several cultures were selected as a result of virtual screening.

An international team of researchers and the Singapore Institute of Bioengineering and Nanotechnology created a biodegradable polymer. The activity of the polymer was tested on cultures of five ESKAPE pathogens, including *Pseudomonas aeruginosa* and methicillin-resistant *Staphylococcus aureus* (MRSA). It turned out that the substance destroys bacteria with 99-100 percent efficiency. Scientists also tested the activity and toxicity of the polymer in mice. The dose of polycarbonate needed for the survival of infected animals was lower or comparable to that of antibiotics for three of the four pathogens.

It is known that aqueous solutions of furatsillin, hydrogen peroxide, povidone-iodine (PVI), chlorhexidine, myramistin, alcoholic solutions of boric acid, liniment of syntomycin, ointment of salicylic acid, levorin, myramistin, chlorhexidine are often used at the local application of medicinal antiseptic drugs. The disadvantage of these drugs is the narrow spectrum of antimicrobial activity, short-term antimicrobial activity, etc.

The paper [7] presents the results of the study of the antimicrobial properties of the antimicrobial agent palisept plus. The high sensitivity of strains of microorganisms (*S. aureus*, *E. coli*, *K. pneumoniae*, *P. aeruginosa*) to this drug is shown. According to the author's team, the palisept plus on the oral medication ecamotoxin provides an effective antimicrobial action for a long time.

Additional improvement of good antimicrobial activity of 4-thiazolidine was confirmed in another study [11].

Pharmacological screening of antimicrobial activity of synthesized isomanes is carried out.

Identified compounds with the expressive antimicrobial effect that can increase the sensitivity of clinical strains *S. aureus* and *S. Haemolyticus* to oxacillin, which can be used to create new combined antimicrobial chemotherapeutic agents.

Chinese, American and Singapore researchers [12] have synthesized a substance with antimicrobial properties that effectively destroys ESKAPE-bacteria, which was resistant to most antibiotics. The acronym ESKAPE combines the names of pathogens that are highly resistant to most antibiotics and cause most hospital infections worldwide.

Chemists and biologists synthesize antimicrobial peptides and polymers. Despite the efficacy and broad spectrum of action, antimicrobial peptides are toxic, and their production is rather expensive. Most of the described antimicrobial polymers are not decomposed and therefore can accumulate in the body and eventually become toxic. In addition, until now, their activity in living organisms has not been practically studied.

Despite the fact that scientists are constantly synthesizing new generations of drugs, bacterial resistance is still a significant problem.

The antimicrobial activity of the developed dermatological ointment with a two-phase extraction of black poplar kidneys using the method of diffusion into agar (the method of "wells") was studied [14]. As test cultures, eleven different strains of microorganisms were used. The results of microbiological studies have shown that the biphasic extracts of black poplars and ointment on its basis have a expected antimicrobial action against pathogenic microorganisms.

The study was conducted to evaluate the in vitro antibacterial activities of 18 essential oils chemotypes from aromatic medicinal plants against streptococcus *S. Pyogenes* [15].

The chemical composition of oil was analysed by GC and GC-MS. the reducing power, antioxidant and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical-scavenging activities of the essential oil were studied. The reducing power was compared with ascorbic acid, and the other activities were compared with 2,6-di-tert-butyl-4-methyl phenol (BHT, butylated hydroxytoluene). The results showed that the activities were concentration dependent. The antioxidant activities of the oil were slightly lower than those of ascorbic acid or BHT, so the oil can be considered an effective natural antioxidant. Antimicrobial activities of the essential oil from the leaves of *Origanum syriacum* was also determined on 16 microorganisms tested using the agar-disc diffusion method, and showed antimicrobial activity against 13 of these.

Antibacterial activity of essential oils was investigated using disc diffusion method. Minimum Inhibitory Concentration of essential oils was measured using broth dilution method. Out of 18 essential oils tested, 14 showed antibacterial activity against *S. pyogenes*. Among them *Cinnamomum verum*, *Cymbopogon citratus*, *Thymus vulgaris* CT thymol, *Origanum compactum*, and *Satureja montana* essential oils exhibited significant antibacterial activity. The in vitro results suggest that, for patients (if aromatherapy is used) these essential oils, considered as potential antimicrobial agents, should be preferred.

The authors plan additional studies of essential oils in clinical strains regarding the potential clinical use in therapeutic therapy (to determine whether they can effectively replace antibiotics or may be used in combination) [18].

Adiantum Linn. of *Adiantaceae* family is one of the most common and widely distributed species. Ethnomedicinally, the genus is important and popularly known as "Hansraj" in Ayurvedic System of Medicine.

In the present study its four important species, i.e. *Adiantum capillus-veneris*, *Adiantum peruvianum*, *Adiantum venustum* and *Adiantum caudatum* were collected and extracted with methanol. These extracts were tested for their antimicrobial agents against five gram positive, six gram negative (including multiresistant bacteria *Staphylococcus aureus*) and eight fungal strains using standard microdilution assay. The maximum activity was exhibited by the methanolic extract of *Adiantum venustum* followed by *Adiantum capillus-veneris*, *Adiantum peruvianum* and *Adiantum caudatum*. The methanolic extract of *Adiantum capillus-veneris* had very low MIC value (0.48 µg/ml) against *Escherichia coli* whereas, *Adiantum venustum* extract against *Aspergillus terreus* with MIC of 0.97 µg/ml. Total phenolic constituents of *Adiantum* species viz. *Adiantum venustum*, *Adiantum capillus-veneris*, *Adiantum peruvianum* and *Adiantum caudatum* were 0.81% (w/w), 0.83% (w/w), 0.71% (w/w) and 0.52% (w/w), respectively (as gallic acid equivalent); implying that the observed activity could be related to the amount of phenolics [19].

In [16], the authors studied antimicrobial activity of lipophilic complexes obtained from *Galium* species. The study was conducted in vitro by agar diffusion. *Staphylococcus aureus* was found to be the most susceptible to the studied lipophilic complexes. *Escherichia coli* and *Proteus vulgaris* showed low sensitivity. *Pseudomonas aeruginosa* and *Bacillus subtilis* showed moderate sensitivity. The obtained results provided the basis for

further in-depth studies of the antimicrobial and antifungal activity of the lipophilic complex of the genus *Galium* L.

The exponential growth of bacterial resistance to antibiotics raises a problem for clinicians regarding endophthalmitis in postcataract surgery through multidrug-resistant (MDR) organisms. Treatment options are limited and the results are bad. Therefore, prompt surgical prophylaxis provides the best treatment solution. There are currently no recommendations for surgical prophylaxis in patients with bacterial colonization of multi-resistant (MDR) organisms.

The current ESCRS (European Society Cataract and Refractive Surgery) recommendation for a 3-minute exposure to 5%PVI is effective for gram-negative bacteria and most gram-positive cocci. However, 5%PVI is ineffective for enterococci and requires exposure to chlorhexidine for 5 minutes.

Materials and methods

Materials

Strains of Gram-positive and Gram-negative microorganisms, were used: *S. aureus* (ATCC 6538), *S. saprophyticus* (ATCC 15305), *E. coli* (ATCC 25922), *P. aeruginosa* (ATCC 9027). The density of the microbial suspension was determined according to the standard of turbidity 0,5 by McFarland (equal to 1.5×10^8 colony-forming units (CFU)/ml).

The study used samples of the KTIOL-BF series. These functional and antioxidant drugs have been obtained on the basis of the systemic concept of health. As model samples, the preparations of the KTIOL-BF (biologically functional) series were used. The preparations KTIOL-BF5, KTIOL-BF6 and KTIOL-BF7 are based on plant extract and iodine solution. The preparations KTIOL-BF25, KTIOL-BF26 and KTIOL-BF27 on the basis of plant and on the basis of plant and animal extracts and solution of nanosized particles of colloidal silver. KTIOL-BF49 based on plant and animal extract and KTIOL-BF69 on the basis of plant extract and iodine solution.

The preparations KTIOL-BF31 and KTIOL-BF32 are based on a two-phase plant extract. The preparations KTIOL-BF36, KTIOL-BF37, KTIOL-BF38 and KTIOL-BF39 on the basis of plant extract and iodine solution. Povidone-iodine, PVI (pharmaceutical preparation BETADINE is based on a solution of povidone-iodine, surface-active and auxiliary substances) and Chlorophyllipt (CHL) based on two phases of plant extract were used as controls.

Order of conducting researches

Analysis of the methodology. Preparation of exploratory strains of Gram-positive and Gram-negative microorganisms, model preparations of the KTIOL-BF series and control drugs. Execution of planned research, processing and discussion of the results, conclusions.

Description of the methodology

As the references, strains of Gram-positive and Gram-negative microorganisms, were used: *S. aureus* (ATCC 6538), *S. saprophyticus* (ATCC 15305), *E. coli* (ATCC 25922), *P. aeruginosa* (ATCC 9027). The density of the microbial suspension was determined according to the standard of turbidity 0,5 by McFarland (equal to 1.5×10^8 colony-forming units (CFU)/ml) [14].

An antimicrobial activity of drug samples were determined by the agar-well diffusion method. In one Petri dish the activities of four or five different samples were studied. The investigated samples were dissolved in formamide in a ratio of 1:10. 10 ml of a sterile melted meat peptone agar (MPA) was poured into a Petri dish. After cooling of this medium layer, sterile glass cylinders were placed in it (height 10 mm, internal diameter 6 mm) and then 15 ml of melted MPA mixed with overnight suspension of the test-microbe were added. When the second layer of medium became solidified, the cylinders were removed and into the wells that were formed, the 0,5 μ l of the drug samples were delivered under the aseptic condition. After incubation period for 24 hours at 37 °C the results were determined. The the inhibition zones (no growth) of the test-microorganisms around wells were measured in millimeters.

Working out of research results

According to the diameter of the microbial growth inhibition zone the degree of a susceptibility of microorganisms to the antibacterial solutions were adopted: as high susceptible to drug sample – if the diameter of the growth inhibition zone of microorganisms exceeded 20 mm; susceptible if the diameter was from 14 to 20 mm; and low susceptible - from 8 to 14 mm. All tests were performed triplicate and average values were recorded.

After the second layer of the agar was sealed, the cylinders were also removed in the formed wells; the samples of the investigational drugs were 0.3 \pm 0.03 ml. In one cup, Petri studied the activity of four or five different samples.

The seeds were incubated at 37 °C. for 48 hours. The results were determined in the presence of zones of growth retardation test-microorganisms, which were clearly visible around the walls.

By the degree of sensitivity of microorganisms to antibacterial solutions, we measured the diameter of the zone of suppression of microorganisms.

As a scientific and practical basis in the planning and implementation of this study, the systemic concept of health [3] was used. This concept includes two systems of KTIOL.

Results and discussion

Taking into account the principles of the systemic concept of health and the physiologically functional system of KTIOL-II, samples of type KTIOL-BF [2, 8] included hydrophilic lipophilic extracts from plant and/or animal raw materials, antioxidants, biologically active and auxiliary components. The results of the study are presented in Tables 1 and 2.

The analysis of the data in Table 1 in comparison with the control sample PVI the following. From samples KTIOL-BF5, KTIOL-BF6 and KTIOL-BF7 on the basis of initial extracts only sample KTIOL-BF7 provided an initial good effect on all microorganisms being studied.

When the nanoparticles of colloidal silver were introduced into the original extracts (KTIOL-BF5, KTIOL-BF6, KTIOL-BF7), specimens KTIOL-BF25, KTIOL-BF26 and KTIOL-BF27 were respectively obtained. Colloidal silver slightly reduced the antimicrobial effect of these samples on *S. aureus* and samples KTIOL-BF26 and KTIOL-BF27 relative to *S. saprophyticus*. Note that only a sample of 25 nanoscale colloidal silver showed a good antimicrobial effect on the microorganisms *S. Saprophyticus*, *E. coli*, *P. aeruginosa* examined.

Table 1
Antimicrobial properties of samples of model_drugs KTIOL-BF on the basis of extracts
(in mm, retarded growth zone)

Drug samples	Growth inhibition, mm (Mean ±SD)			
	<i>S. aureus</i>	<i>S. saprophyticus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>
Control PVI	10±0.2	12±0.5	10±0.4	12±0.2
KTIOL-BF5	0	0	0	0
KTIOL-BF6	14±0.5	12±0.8	0	0
KTIOL-BF7	14±0.3	14±0.6	18±0.5	14 ±0.4
KTIOL-BF25	12±0.7	16±0.4	18±0.6	16±0.5
KTIOL-BF26	12±0.5	12±0.4	18±0.5	20±0.5
KTIOL-BF27	12±0.4	12±0.3	14±0.8	20±0.6
KTIOL-BF49	16±0.4	16±0.5	22±0.6	24±0.8
KTIOL-BF69	18±0.6	16±0.3	14±0.3	18±0.6

Table 2
Antimicrobial properties of samples of model drugs KTIOL-BF on the basis of extracts with
biologically active components (in mm, retarded growth zone)

Drug samples	Growth inhibition, mm (Mean ±SD)			
	<i>S. aureus</i>	<i>S. saprophyticus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>
KTIOL-BF31	20±0.4	18±0.5	18±0.5	18±0.3
KTIOL-BF32	24±0.6	18±0.6	30±0.5	16±0.4
KTIOL-BF36	20±0.6	18±0.5	18±0.7	18±0.4
KTIOL-BF37	16±0.5	16±0.7	22±0.4	12±0.5
KTIOL-BF38	24±0.2	22±0.6	30±0.8	20±0.7
KTIOL-BF39	14±0.4	14±0.5	20±0.6	16±0.6
control 52	10±0.3	12±0.4	10±0.4	10±0.4

Also modified and samples 49 (based on the iodine content extract 7) and 69 (based on the iodine content extract 6 and plant extract) were also studied. Sample KTIOL-BF49 showed a good antimicrobial effect on all microorganisms studied. Sample KTIOL-BF69 (Improved Sample KTIOL-BF6) neutralized the defects of sample KTIOL-BF6 and provided antimicrobial effect on all microorganisms under study.

The analysis of the data in Table 2 in comparison with the control sample 52 (pharmaceutical preparation Chlorophyllipt on the basis of a two-phase plant extract) revealed the following. Samples KTIOL-BF31 and KTIOL-BF32 on the basis of two-phase plant extracts provided a very good integral antimicrobial effect on all investigated microorganisms: *S. aureus*, *S. saprophyticus*, *E. coli*, *P. aeruginosa*. For the first time, a high antimicrobial effect of samples KTIOL-BF32 and KTIOL-BF38 on strain *E. coli* was detected.

Modified model samples KTIOL-BF36, KTIOL-BF38 and KTIOL-BF39 (were also studied. Samples KTIOL-BF37 and KTIOL-BF39 showed a good antimicrobial effect on all microorganisms being studied.

The high integral sensitivity to the sample of the preparation KTIOL-BF38 was revealed by all strains of microorganisms examined (the diameter of their growth delay

exceeded 20 mm). Also the possibility of a high antimicrobial action on the E. coli strain (growth delay diameter of 30 mm) was confirmed. Also, the possibility of a high antimicrobial action on E. coli strain (diameter growth delay of 30 mm) was confirmed. This is due to the complex action of the drug KTYOL-BF38 on the study of gram-positive and gram-negative strains of microorganisms.

Conclusions

On the basis of analytical and experimental research new data on the antimicrobial properties of samples of model preparations of KTIOL-BF on the basis of two-phase extracts from animal and plant raw materials were obtained.

For the first time the possibility of high antimicrobial action of samples of the preparation of KTIOL-BF32 and 38 on the E. coli strain (30 mm growth retardation diameter) was confirmed.

It was found that samples of the KTIOL-BF model preparations compared with the control agents (BETADINE /PVI, Chlorophyllipt) showed higher and good antimicrobial properties for S. Aureus, S. Saprophyticus, E. coli, P. Aeruginosa and integral strains.

The obtained data confirmed the expediency of further in-depth studies of antimicrobial and antifungal activity of hydrophilic and/or lipophilic drugs of a number of KTIOL in the systemic concept of health, in particular in the treatment of ophthalmic and gerontological prophylaxis, treatment and rehabilitation.

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Functional-technological properties of protein composite of animal origin

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Abstract

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Introduction. The purpose of the study is to study the functional and technological properties of the obtained protein compositions from poultry meat and to determine the optimum with high quality indices.

Materials and methods. The meat of mechanical treatment, fillet of poultry, hams with skins were studied, which were subjected to microwave-vacuum drying with humidity not more than 5% and prepared samples – Mepro 85 (the Dutch manufacturer) - animal protein of cattle and Sunprotein - vegetable protein.

Results and discussion. The obtained results indicate that the resulting dry powders can bring the finished product closer to a product with a balanced composition, high quality and nutritional value. It has been studied that specimens from the fillet of poultry, hams with skins, and meat of mechanical treatment of poultry contained more than 80–96% free moisture, which gives the product its use with greater juicy and tender consistency.

At the same time, the best water-retaining ability in the sample from the fillet of poultry is 10.2% and in Sunprotein - 11.4%. The greatest fat-retaining ability was the meat of mechanized treatment of poultry – 13.1% compared to the sample Mepro 85 – 5.25%. The emulsifying ability in the sample meat of mechanical treatment of poultry is 73%, which is 20–25% higher compared to other samples.

As a result of microbiological research no bacteria of the colon germ, pathogenic microorganisms, including the genus *Salmonella*, sulfite-reducing clostridia were found. The total amount of microorganisms after drying in all samples does not exceed the norm for boiled dried meat 5×10^3 . The best result was observed in the sample Sunprotein – 1.8×10^3 .

In the sensory analysis, it has been found that the sample of the fillet of poultry has a better outer look and smell, while the consistency is better in meat of mechanical treatment of poultry. It is the most crumbly, inherent in dry powders.

Conclusions. The comparative analysis confirms the high functional and technological properties of samples from the fillet of poultry and meat of mechanical treatment of poultry, as well as being safe for use in meat products.

Introduction

The growing standard of living of the population in the conditions of deficiency of animal proteins has led to the intensive development of new trends in meat products, which consists in optimal combination of both meat and non-meat protein-containing food components for obtaining high-quality and biologically valuable foods. [9].

In the meat industry, animal and vegetable protein preparations are used not only as functional additives, which help increase the yield of traditional meat products, but also as the formulation components of combined meat products (milk protein preparations, soybean isolates, protein hydrolyzates, hydrocolloids etc.) [5].

Many scientists contributed significantly to the development of rational approaches to adequate replacement of meat raw materials with protein-containing and non-protein fillers, to improve the indicators of food and biological value and biological efficiency of meat products, their technological characteristics and cost-effectiveness [4]. They are: V.M. Pasychny, R. Tarte, E. Tornberg, P.A. Lofgren, A.I. Zharinov, N.A. Yancheva, M.M. Klimenko, A.Yu. Sokolova and other scientists [10].

Swedish scientist E. Tornberg was engaged in the development of milk protein preparations that had functional and technological properties similar to meat raw materials [2]. American scientist P.A. Lofgren was involved also in the development of milk protein preparations, namely casein sodium [3]. Such a technology has a limited range of applications, since there are people with lactose intolerance.

Arihara K. and Carballo J. were involved in the development of sausage products with the addition of dry meat powder. Campbell R. E., Hunt M. C. studied the methods of drying beef, but the disadvantage of their method is that the product was characterized by increased rigidity and low quality.

Taking into account that the proposed raw material, namely poultry meat, is a product that is rapidly spoiled, the production of a dry meat additive is promising to increase functionality, stability in storage and transportation. The use of modern technology helps to get products with a high content of high quality protein, high quality of products and nutritional value.

The development of technology of meat products with a dry meat additive is associated with the involvement of different types and grades of meat, as well as combining it with plant fillers, the development of innovative methods of drying and packaging products aimed at increasing the consumer properties and hygienic quality of products.

According to the results of previous studies, namely the use of different methods of meat drying (sublimation, infra-red, lyophilic, microwave-vacuum drying, drying with combined heat approach, etc.), it was established that one of the ways of preserving meat protein in the native state is drying at low temperatures, namely, the use of microwave-vacuum drying [16]. Such drying leads to the release of a large amount of heat, which is spent solely on the evaporation of moisture without heating the fabric of the product, and as a result evaporation can occur at a low temperature [1]. This contributes to intensive evaporation of moisture without significant change in the structure of the surface layer, reducing the duration of processing, preservation of biologically active components of raw materials, dying of microbial cells and inactivation of enzymes.

The purpose of this research was to investigate the functional and technological properties of the received protein compositions from poultry meat and to determine the optimum with high quality indices.

Materials and methods

Materials

The following objects of research were used: meat of mechanical treatment, fillet, hams with skins, which were subjected to microwave-vacuum drying. The following comparisons were used foreign counterparts Mepro 85 (the Dutch manufacturer) - animal protein from cattle and Sunprotein (USA) - vegetable protein. [16, 18]. The drying was carried out at a temperature of not more than 37°C to obtain the required mass of condensate at constant stirring [6].

Determination of moisture content

The moisture content of the protein component was determined by drying the crushed sample at a temperature of 150°C for 1 hour. The mass fraction was determined as the difference between the weight of the drying unit (A1) and after drying (B) to the weight of the weight gain (A), expressed as a percentage:

$$W = (A_1 - B) / A \times 100$$

Determination of the number of MAOAM

Determination of mesophilic aerobic and optional anaerobic microorganisms was carried out using a deep sowing method based on seeding of product dilutions into a dense nutrient medium.

At 1 cc. From each breeding place are put on the bottom of two sterile Petri cups, slightly opening them. Then, in each cup, pour 15-20 cubic centimeter of molten and cooled to 45 °C of nutrient agar with yeast extract and glucose are poured, then the cup is stirred along the surface of the table with circular motions [10]. After cooling the agar, the cups are placed in the thermostat upside down at 30 °C for 72 hours. Then the calculation of all types of colonies is conducted.

Drying process

The studies were carried out in a sealed reactor of a radio-transparent material (glass). Vacuum in the chamber is provided by a membrane vacuum pump. The reactor is placed in a chamber with a microwave energy source. The vapor volume of the chamber was communicated with the condenser where cold water circulated. Steam was converted into condensate, and the mass of condensate was determined by means of digital scales [16]. The moisture content of the raw material was established by the mass of the condensate. The temperature of the reactor was measured with a radiation pyrometer, and the pressure in the chamber was measured with a vacuum gauge. The consumed electric energy was determined with the help of a meter.

Determination of water-absorbing ability

The water-binding ability of meat was determined by the Grau and Hamma method. A weight of the mass of 0.3 g, weighed to 0.0001 g precision on a polyethylene with a

diameter of 55-60 mm is transferred to an ash-free filter, which is placed on a Plexiglas plate 100×100 mm in size. The hard cover is covered with another plate of the same size and a load of 1 kg is placed on top. The pressing lasts for 10 minutes, after which the contour marks the spots around the pressed meat. The area is measured by a planimeter in cubic centimetres. The content of bound water in meat is calculated by the formula:

$$V = (A-K \times B)/M \times 100$$

A-water content in weight, mg; K = 8.4 mg; B- area of a wet spot, cm^2 , M-the mass of weight meat, mg.

Determination of water-retaining capacity

The protein component is hydrated in distilled water at a ratio of 1: 5 for 1 hour, then it is placed in a thermostat with a temperature of 74-76 °C and kept for 15 minutes. The contents of the glasses are transferred to centrifuge nets and centrifuged for 15 minutes at 1000 rpm for separation of unbound water. It is calculated as the difference between the mass of the hydrated texture (Mr) and the mass of dry (Ms) to the mass of dry texture (Ms), expressed as a percentage:

$$\text{WRA} = (\text{Mr}-\text{Mc})/ \text{Mc} \times 100$$

Determination of fat-retaining ability

The protein component is dispersed in 10 g of vegetable oil and for 1 h at 20°C, then placed in a thermostat with a temperature of 74-76 °C and kept for 15 minutes. The contents of the glasses are transferred to centrifuge mesh and centrifuged for 15 minutes at 1000 rpm. Calculated as the difference between the mass of the dispersing texture (Mr) and the mass of dry (Ms) to the mass of the dry texture (Ms), expressed as a percentage:

$$\text{FRA} = (\text{Mr}-\text{Mc})/ \text{Mc} \times 100$$

Results and discussion

Determination of microbiological indicators

Experimental studies were conducted with dry protein concentrate on the following indicators: microbiological, physico-chemical and sensory [7, 8].

The first point of control is the determination of the sanitary state of the powder after its preparation.

Microbiological contamination of the samples was determined before and after drying (Figure 1). According to the results of the obtained data, it was determined that the total number of microorganisms after drying in all samples did not exceed the norm for boiled dried meat 5×10^3 , as well as no bacteria of the colon germ, pathogenic microorganisms, including the genus *Salmonella*, sulfite-reducing clostridia were found. That is, dry meat additives comply with standard, do not exceed the permissible level and are safe for use in meat products.

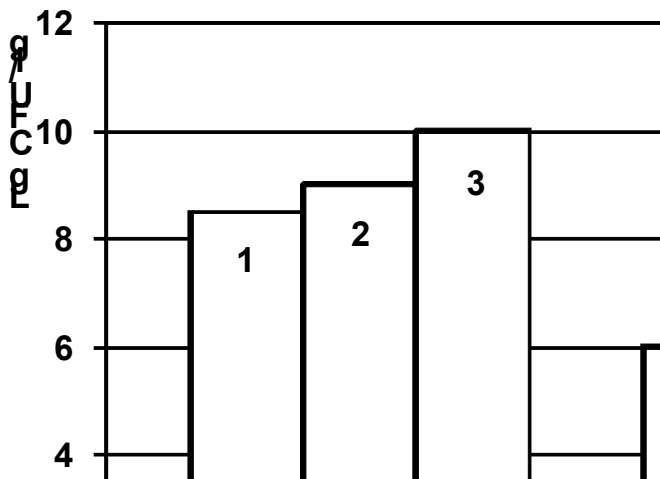


Figure 1. Lg colony-forming units/1 g protein component:
1 – Chicken Fillet, 2 – Chicken Ham, 3 – MMT, 4 – Sunprotein, 5 – Meopro 85, 6 – Standard.

Determination of functional and technological indicators

The next stage of the research was the study of the functional and technological properties of all experimental samples namely: moisture content after drying, water-binding ability, water-retaining ability, fat-retaining ability and emulsion stability.

The result of determining the moisture content after drying in the samples studied is different, which is due to their composition and the effect of heat treatment in the drying stage, as well as the properties of raw materials [15].

At the mechanical action of high pressure on muscle fibers of poultry meat, there occurs a destruction of myofibrils with the release of myofibrillar proteins. This is accompanied by a rupture of electrostatic bonds and the formation of ionized groups that bind water [12].

On the basis of the data obtained, it can be concluded that the emergence of additional centers available in water after treatment by pressure, promotes the increase of moisture absorbing ability in poultry meat.

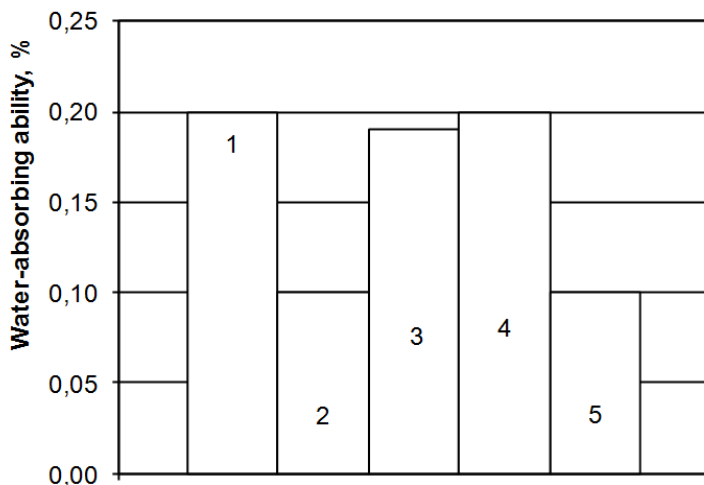


Figure 2. Moisture content of the protein component after drying:
1-Chicken Fillet, 2-Chicken Ham, 3-MMT, 4-Sunprotein, 5-Mepro 85.

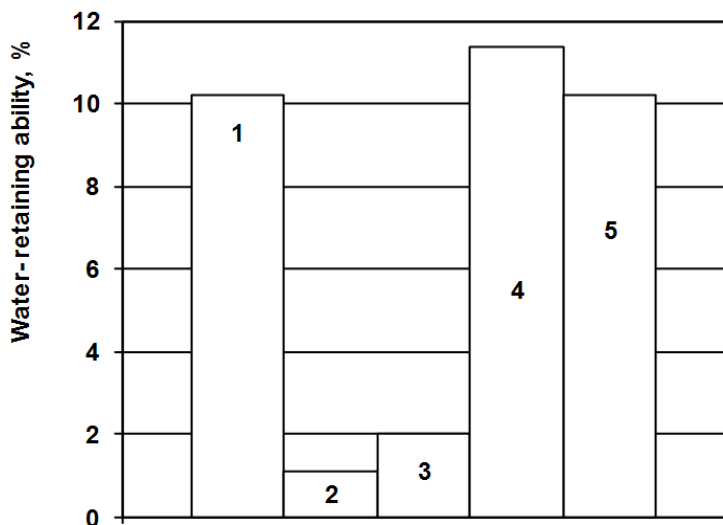


Figure 4. Content of water-retaining ability of the protein component after drying:
1 – Chicken Fillet, 2 – Chicken Ham, 3 – MMT, 4 – Sunprotein, 5 – Mepro 85.

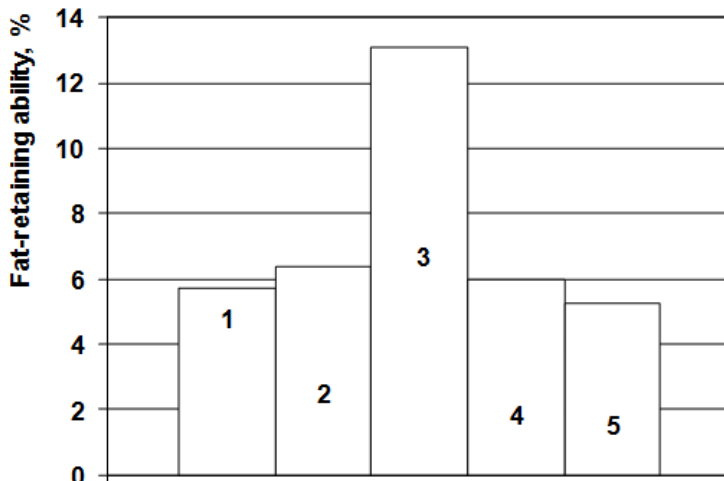


Figure 5. Content of fat – retaining ability of the protein component after drying:
1 – Chicken Fillet, 2 – Chiken Ham, 3 – MMT, 4 – Sunprotein, 5 – Mepro 85.

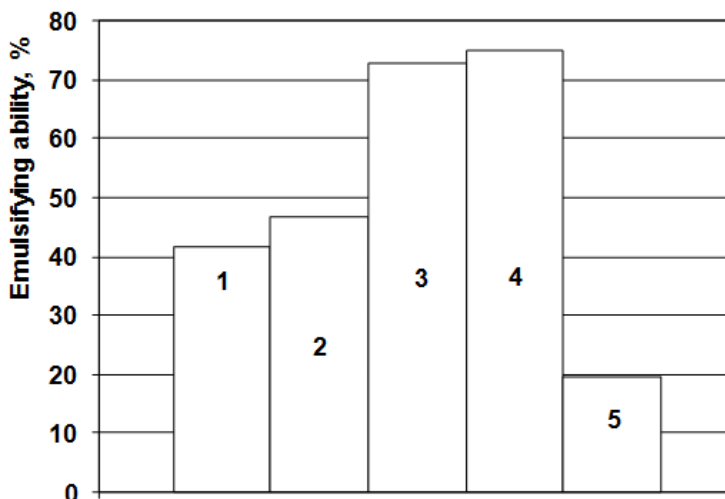


Figure 6. Content of emulsifying ability of the protein component after drying:
1 – Chicken Fillet, 2 – Chiken Ham, 3 – MMT, 4 – Sunprotein, 5 – Mepro 85.

The value of water-retaining, fat-retaining and emulsifying ability in the samples varies, due to their composition and the effect of heat treatment in the drying stage. Comparing all the studied samples of meat supplements studied as protein filler, we see that the highest results were found in chicken fillet and meat of mechanical processing, the lowest observed in chicken ham [14].

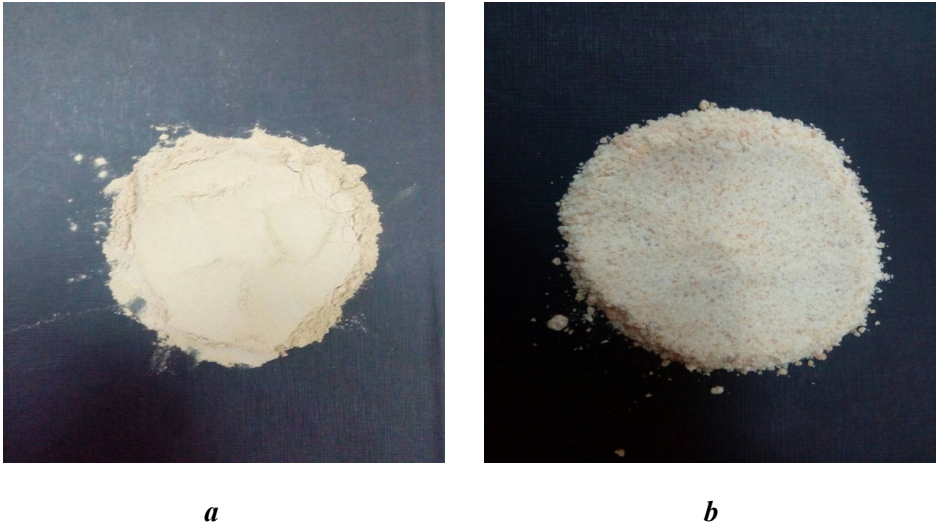


Figure 7. The samples of the protein component after drying: a- MMT, b- Sunprotein

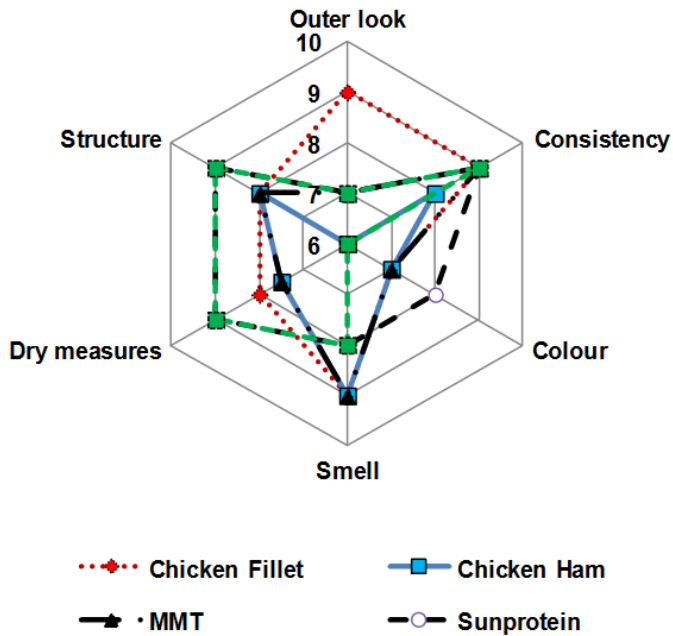


Figure 7. Profilogram of the studied meat additives

According to the sensory evaluation, model meat supplements were characterized by high sensory characteristics [2]. Loose consistency, inherent in dry powders, homogeneous color, like meat, pleasant scent. The best sensory properties were found in chicken fillet, mechanical collapse meat and sunprotein, the lowest rates were observed in the chicken ham.

Conclusion

1. Based on the analysis of existing technologies for the production of protein supplements from various anatomical parts of poultry meat, the technology of dry additives with the use of electromagnetic energy sources of ultrahigh frequency under vacuum was developed.
2. In work was investigated of efficient use of meat additives in meat products is investigated, to compare different samples according to microbiological, physical-chemical and functional-technological indicators.
3. It is shown that the highest rates were observed in dry powders of chicken fillet and mechanically-processed meat, which will bring the finished product closer to a product with a balanced composition, high quality and nutritional value.
4. Based on the results obtained and from an economic point of view it is more appropriate to use dry powder from mechanical collapse meat.
5. It has been experimentally established that the protein composition of animal origin obtained by the proposed method meets the existing technological regulations.

Regulation EU No. 178/2002 requires enterprises to identify from whom raw materials and ingredients and have a traceability system and procedures that allow them to quickly obtain the necessary information. As a result, the use of the developed additive allows you to create meat products controlled by origin.

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Identification, characterization and industrial utilization of autochthonous strains of *Streptococcus thermophilus* isolated from Moldavian raw milk and dairy products of spontaneous fermentation

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Abstract

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Introduction. Lactic acid bacteria with known metabolic properties contribute to the sensory characteristics of the products, to their quality and safety. The limited number of highly biotechnologically available strains and the constant risk of bacteriophage attacks justify the continued searching for new strains.

Materials and methods. Identification of thermophilic lactic acid bacteria was performed on the basis of phenotypic properties and using molecular methods – RAPD-PCR and FTIR spectroscopy. Antagonistic activity of selected strains was carried out by diffusion method. Starter culture and samples of yoghurt were manufactured according to the traditional technology.

Results and discussion. Selected strains of *S. thermophilus* are characterized by intense acidification of the milk for 3–4 hours, developing a milk acidity between 65–74 °T, forming a homogeneous, compact, dense coagulum, which ensures its firm consistency. The strains *S. thermophilus* strains CNMN-LB-50 and CNMN-LB-51 are capable of synthesizing exopolysaccharides (EPS).

The antagonistic activity against pathogenic microorganisms of strains of is high. The inhibition range varies between 16 and 18 mm from *Escherichia coli*. and 19–21 mm to *Staphylococcus aureus*, which inhibits the development of intestinal infections and prevents the development of pathogens in fermented milk samples. The maximum yield of EPS synthesized at suboptimal temperature of 32 °C is 19.4% higher than at the optimal temperature for this process (40 °C) for *S. thermophilus* CNMN-LB-50 strain and 23, 8% for *S. thermophilus* CNMN-LB-51 strain. To stimulate the synthesis of EPS under industrial conditions in the manufacture of fermented milk products without altering the temperature, the nutrient medium should be supplemented with sucrose in an amount of 8%.

Conclusions. It is possible obtaining from the microflora of raw milk and dairy products of spontaneous fermentation the autochthonous strains of lactic bacteria with valuable biotechnological properties, intended for use in the composition of starter cultures for the production of fermented milk products.

Introduction

At the present, technological processes based on the activity of lactic acid bacteria (LAB) have a special significance. Modern dairy production is closely linked to the search and selection of suitable LAB with the specific properties, which implies an increase in the diversity of fermented dairy products. Thermophilic and mesophilic LAB are the most widely used as starter cultures for the production of fermented dairy products. The specific taste, consistency and other properties of the fermented dairy products depend on the strains which starter culture made up. The thermophilic LAB are capable to grow at temperatures of 37-45 °C that is an important condition associated with the technological process of manufacturing fermented dairy products such as yoghurt, baked fermented milk and various cheeses and play an important functional role in fermented dairy products [1].

Thermophilic cocci strains isolated from raw milk and spontaneous fermentation dairy products, in most cases, belong to *Streptococcus* and *Enterococcus* genera. Thermophilic LAB *S. thermophilus* are "useful" representatives for their application in starter cultures [2].

Identification process of an isolated strain includes its complete description and comparison with a reference strain. The rapid and specific classification of bacteria is an important task in microbiology, which can be achieved using traditional methods based on physiological, biochemical and molecular methods.

However, many scientists notice difficulties in differentiating and identifying of *Streptococcus* and *Enterococcus* bacteria using only the phenotype classification methods describing the inadequacy of the classical phenotype characteristics of these genes, such as the ability to grow on a medium containing esculin, bile and sugar fermentation, antibiotic resistance, and the range of typical growth temperature [3–5].

The aim of the present study was isolation and identification of *S. thermophilus* strains from raw milk and spontaneous fermentation dairy products and to study their industrial potential in order to create starter cultures which are suitable to yogurt production in local conditions.

Materials and methods

Reference bacterial strains

The following strains *Streptococcus thermophilus* A737 was obtained from Czech Collection of Microorganisms (Brno, Czech Republic), *Streptococcus thermophilus* 1241, *Lactobacillus casei* 4791 were obtained from Collection of Microorganisms (Food Research Institute, Bratislava, Slovakia).

Isolation

10 grams of samples were homogenized with 90 ml sterile peptone physiological saline solution (5 g peptone, 8.5 g NaCl, up to 1000 ml distilled water, pH 7.0). The homogenate was diluted serially and the appropriate dilutions were surface plated on M17 agar media (Merck, Darmstadt, Germany), then plates were incubated at 37 °C for 72 hours.

Physiological and biochemical tests

Morphology. Pure cultures grown in skimmed milk in an incubator at 37 °C for 18 h was used. Before a microscope examination smears of cultures were stained with methylene blue for a few minutes.

Production of CO₂. 10 ml of M17 broth culture of the test strain incubated at 37 °C for 18 h covered the surface of the broth by molten overlay agar, precooled to 47 °C ± 1 °C, to a depth of 1 cm. Cultures were incubated for 1 week at 37 °C. The presence of gas is evident when the agar layer detaches itself from the underlying contents.

Catalase reaction. Mixed equal volumes of the M17 broth culture, incubated set at 37 °C for 18 h, with 150 g·l⁻¹ hydrogen peroxide in a tube fitted with a rubber stopper. Gently turn the tube upside down once to favour mixing, and observe for bubbles of oxygen forming in the broth at room temperature over 20 min.

Action in litmus milk. In 10 ml of litmus milk (70 g litmus in 1000 mL skimmed milk) was introduced a loop of studied culture. Litmus milk acidified by *S. thermophilus* turns pink and then coagulates. After coagulation the colour remains pink due to very slow and often incomplete reduction of litmus, with a more intensely coloured upper ring.

Thermoresistance. Into 5 ml of skimmed milk by loop was introduced studied strain, incubated set at 37 °C for 4 h. After, the tubes were placed in the water bath at temperature of 60 °C for 30 minutes, and then cooled. Finally, the samples were incubated at 37 °C for 24 h. Acidified or coagulated milk means thermoresistance of studied strains.

Growth in the presence of sodium chloride. Inoculated tubes containing M17 broth with 20 g·l⁻¹ and 40 g·l⁻¹ NaCl incubated for 7 days at 37 °C. Presence of turbidity in the tube indicates the culture growth.

Growth in the presence of methylene blue. Inoculated skim milk supplemented with 0.1 g·l⁻¹ and 1.0 g·l⁻¹ of methylene blue solution were incubated at 37°C. Coagulation or its absence was visually determined at 12, 24 and 48 h. for 48 h. *S. thermophilus* does not grow in presence of methylene blue.

Growth at pH 9.6 was observed after 48 h of incubation at 37 °C in M17 broth which pH was adjusted to 9.6.

Isolation of EPS. 100 ml of yoghurt were centrifuged at 837 rad·s⁻¹ for 10 min and 17 ml of trichloroacetic acid (Chimprom, Ukraine) were added to each sample. Samples were cooled up to 4°C and again centrifuged at 837 rad·s⁻¹ for 10 min. Precipitation of EPS from samples was provided using cold ethanol (1:3). The samples were kept in the fridge for 24 h and then centrifuged (40°C, 837 rad·s⁻¹, for 10 min).

(GTG)₅-PCR fingerprinting

Total genomic DNA was extracted from the colony material of each strain after incubating them for 24 h in M17 broth (Merck, Darmstadt, Germany) at 37°C. DNA was extracted from 1 ml of the broth centrifuged at 5000×g for 10 min. A loop of culture was transferred to 1 ml of distilled water, mixed and centrifuged at 10000·g for 5 min. InstaGene suspension (Bio-Rad, Hercules, California, USA) was added to the sediment and incubated at 56 °C for 25 min. Then the mixture was vortexed, incubated at 100 °C for 8 min, vortexed, centrifuged at 10 000 ×g for 5 min and the supernatant containing DNA was removed. A volume of 2 µl of the DNA solution was added to the Polymerase Chain Reaction (PCR) reaction mixture (total volume, 25 µl) containing 10000 nmol·l⁻¹ (GTG)₅ primer (5'-GTG GTG GTG GTG GTG-3') synthesized by Qiagen (Hilden, Germany), 600 µmol·l⁻¹ dNTP (Applied Biosystems, Foster City, California, USA), 1.5 µmol·l⁻¹ MgCl₂, 1.5 U HotStarTaq DNA polymerase (Qiagen) and 2.5 µl of 10× concentrated PCR buffer supplied with the polymerase. PCR was carried out in a Biometra Personal thermal cycler (Whatman Biometra, Göttingen, Germany) using a thermal programme consisting of the initial denaturation at 95 °C for 15 min, 30 cycles of denaturation at 95 °C for 60 s, annealing at 40 °C for 90 s, ramping at 0.1 °C·s⁻¹, and polymerization at 72 °C for 120 s, followed by the final polymerization at 72 °C for 10 min. A volume of 12 µl of the PCR

product was mixed with 1.5 μl of the loading buffer and analyzed by electrophoresis in a 1.5% agarose gel Seakem LE (FMC Bioproducts, Rockland, Maine, USA) for 5 h at 2.3 $\text{V}\cdot\text{cm}^{-1}$. Molecular size standard $n\times 250$ bp (Invitrogen, Carlsbad, California, USA) was electrophoresed in every fourth lane along with samples. The gel was stained with ethidium bromide for 30 min, destained in distilled water for 5 min, visualized under UV light and photographed with a digital camera. Rep-PCR profiles were compared with reference strains from culture collections.

Sample preparation for FTIR spectroscopy

S. thermophilus strains were cultured in pure cultures in M17 medium for 24 h at 37 °C. The cultures were decimally diluted with 0.9% NaCl and binary mixtures were prepared from the dilution 10^{-4} . A volume of 0.2 ml of the mixture was streaked on M17 agar and the plates were cultured for 72 h at 37 °C. Colonies were picked directly from the plate by an inoculation loop, based on visual evaluation of colony morphology, and each was suspended in 100 μl of distilled water. The suspension containing whole cells was mixed by vortexing for 1 min and 35 μl of the suspension was pipetted on a position on a 96-position Zn-Se plate. The plate was dried for 45 min at 37 °C and immediately measured by Fourier transform infrared (FTIR) spectroscopy.

FTIR spectroscopy

A Bruker Tensor 27 FTIR spectrometer equipped with HTS-XT module (Bruker Billerica, Massachusetts, USA) was used. The spectra were recorded in a range from 4 000 cm^{-1} to 400 cm^{-1} , with spectral resolution of 4 cm^{-1} and 32 scans per sample. The spectra were processed by OPUS software (Bruker Billerica, Massachusetts, USA), which involved averaging of 32 scans, calculation of first derivative by Savitzky-Golay algorithm with 9 smoothing points, and vector-normalization in the region from 1780 cm^{-1} to 720 cm^{-1} . Cluster analysis was carried out by OPUS software on the basis of Euclidean distances using Ward's algorithm, heterogeneities being assigned values from 0 to 2.

Strains employed

Six single-strain cultures were used for starter culture formation: EPS-producing *Streptococcus thermophilus* LB-50 and *Streptococcus thermophilus* LB-51, non-EPS *Streptococcus thermophilus* LB-52, *Streptococcus thermophilus* LB-53, *Streptococcus thermophilus* LB-54 and *Lactobacillus delbrueckii ssp. bulgaricus* LB-42 belonging to the National Collection of Non-Pathogenic Microorganisms of the Institute of Microbiology and Biotechnology (CNMN IMB), previously selected from raw milk. The selected strains were propagated three times consecutively using 0.1% inoculum volume in 10% reconstituted skim milk (InLac, Republic of Moldova) at 40°C until coagulation. Working strains (pure culture 10mL) were gradually associated by inserting into 30 mL of sterile skim milk and incubated at 40°C until coagulation (pH 4.6). Three mixed-strain starter cultures were used to make yoghurt samples for studying the influence of the EPS on the quality of the final product as follows: two EPS-starter culture consists of *S. thermophilus* CNMN-LB-50, CNMN-LB-51 și *Lb. bulgaricus* CNMN-LB-42; *S. thermophilus* CNMN-LB-50, CNMN-LB-52 și *Lb. bulgaricus* CNMN-LB-42 non-EPS starter culture – *S. thermophilus* CNMN-LB-52, CNMN-LB-53, CNMN-LB-54 și *Lb. bulgaricus* CNMN-LB-42. Non-EPS starter culture served as control.

Yoghurt production

Samples of yoghurt were manufactured under industrial conditions using milk produced by JLC Group (Chisinau, Republic of Moldova). The milk was pasteurized at

71°C during 15 s and cooled down to 40°C. Two samples of yoghurt were produced: sample 1 using EPS-producing starter culture and sample 2 with non-EPS starter culture. Samples of yoghurt were incubated at 37°C until pH decreased to a value of 4.5, then kept at 4°C.

Milk acidification. To 10 ml of milk clot was added 20 ml of distillate water, 3 drops of phenolphthalein solution and agitated. Then titrated with a 0.1 mol·l⁻¹ sodium hydroxide solution till the solution has been turned to pink. 1 ml of 0.1 mol·l⁻¹ sodium hydroxide standard solution correspond to 0.009 g lactic acid.

Enumeration of the total viable count of LAB was performed using standard pour plate technique. *S. thermophilus* and *L. delbrueckii subsp. bulgaricus* were incubated aerobically at 37 °C for 48 h. The total counts were expressed as log₁₀ CFU·g⁻¹ of the product.

Antimicrobial activity of selected strains was performed by using disc diffusion method. As the test-culture were used *Staphylococcus aureus* ATCC® 25932™, *Escherichia coli* ATCC® 25922™. Five sterile paper blank discs were placed on the agar plate which was inoculated by indicator strains and the filtered supernatant of *S. thermophilus* strains were applied on the surface of each discs. Plates were incubated at 37°C and zones of inhibition were observed. The inhibition zone was expressed in millimeters.

The viscosity of yoghurt samples was studied with a digital rheometer DV-III (BROOKFIELD, Canada) using the Rheocalc 32 software. Measurements were performed at different rotation speeds up to 21 rad·s⁻¹. The viscosity measurement was carried out at a temperature of 25 °C.

Statistical analysis

Data were expressed as means ± standard deviations for triplicate determination. Statistical analysis was performed using Microsoft Excel 2007. Differences were considered to be significant at validity of $\alpha=0.95$.

Results and discussion

The LAB selection for their use as starter cultures includes the strains isolation from natural sources and study of their properties, which determines the industrial value.

Milk is the most complete medium for selecting LAB. The use of sterile skimmed milk as a culture medium is more favorable for the growing of *S. thermophilus*. Thus, natural selection of industrial valuable strains occurs.

The *Streptococcus thermophilus* strains were isolated from cow's raw milk and spontaneous fermentation dairy product samples collected from local markets in different regions of the Republic of Moldova. Approximately 300 samples were studied for isolation of *S. thermophilus*

S. thermophilus, according to Bergey's Manual [7], are capable of developing at temperature between 42–45 °C. Though, the optimal growth is between 37–40 °C. Therefore all samples were cultivated at 37 °C. At the final of the routine examination of colony morphology and microscopy were selected 5 typical strains *S. thermophilus* for further research.

The 5 selected isolates were initially examined using morphological and biochemical tests (Table 1) and were classified as cocci growing in chains.

All isolates were able to grow at 20 g·l⁻¹ of NaCl content and at 0.1 g·l⁻¹ of methylene-blue in M17 broth. In litmus milk acidified by isolates were observed coagulation and reduction of pink colour. In additional 5 isolates fermented the lactose, saccharose, glucose and not fermented esculine. It is well known that *S. thermophilus* possesses a high ability to grow in a medium supplemented by lactose, glucose and saccharose [8, 9]. Inability to ferment esculine, high sensibility to 40 g·l⁻¹ of NaCl content and lack of grow in 1 g·l⁻¹ of methylene-blue distinguishes *S. thermophilus* species from *Enterococcus* genera [10]. According to the obtained results of morphological and biochemical tests the 5 isolates were identified as *S. thermophilus*.

Table 2

Morphological and biochemical characterization of selected isolates

Characteristics	Code of isolates				
	CNMN-LB-50	CNMN-LB-51	CNMN-LB-52	CNMN-LB-53	CNMN-LB-54
Cell morphology	Cocci in long chains				
Gram staining	+	+	+	+	+
Production of gas (CO ₂)	-	-	-	-	-
Catalase production	-	-	-	-	-
Action in litmus milk	ACR	ACR	ACR	ACR	ACR
Thermoresistance	+	+	+	+	+
Growth in presence of					
NaCl 20 [g·l ⁻¹]	+	+	+	+	+
NaCl 40 [g·l ⁻¹]	-	-	-	-	-
methylene blue 0.1 [g·l ⁻¹]	+	+	+	+	+
methylene blue 1.0 [g·l ⁻¹]	-	-	-	-	-
pH 9.2	-	-	-	-	-
Glucose	+	+	+	+	+
Lactose	+	+	+	+	+
Sucrose	+	+	+	+	+
Galactose	-	-	-	-	-
Maltose	-	-	-	-	-
Ramnose	-	-	-	-	-
Manose	-	-	-	-	-
Sorbita	-	-	-	-	-
Esculin	-	-	-	-	-
Xilose	-	-	-	-	-

+= positive, -= negative

ACR – acidification, coagulation, reduction, Thermoresistance – growth after heating for 30 min at temperature 60 °C.

The PCR product visualization of (GTG)₅ PCR fingerprints are presented in Figure 1.

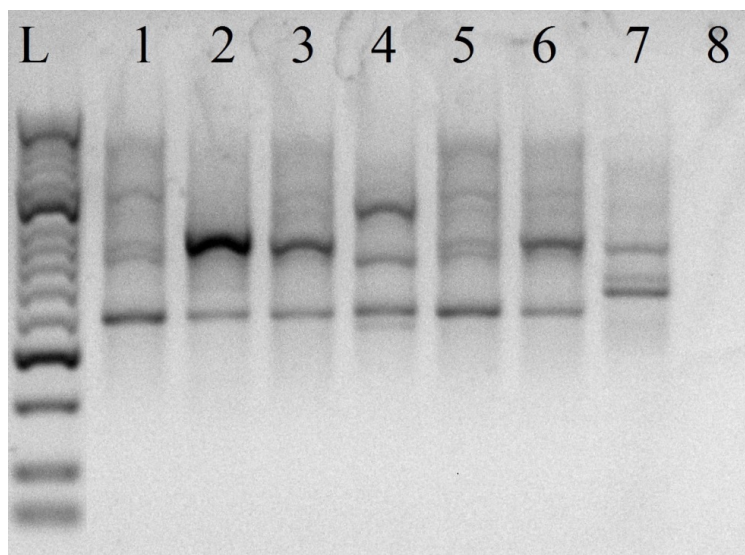


Figure 1. PCR products for *S.thermophilus* isolates

L – HipperLadder 50 bp; 1 – *S. thermophilus* CNMN-LB-52; 2 – *S. thermophilus* CNMN-LB-50; 3 – *S. thermophilus* CNMN-LB-51; 4 – reference strain *S. thermophilus* A737; 5 – *S. thermophilus* CNMN-LB-54; 6 – *S. thermophilus* CNMN-LB-53; 7 – positive control (*S. thermophilus* 1241); 8 – negative control

DNA fragments were yielded 2 to 7 bands. The results confirmed that the similarity level of the genes of the studied strains was 99% with the reference strains of *S. thermophilus*.

The FTIR spectra of the 5 isolates were compared with the reference strain *S. thermophilus* A737. The Pearson product-moment correlation coefficient was applied to the studied strains across the spectra region from 4000 cm⁻¹ to 500 cm⁻¹ [11]. Naumann established that the highest strain correlation is reached at the following intervals: from 3000 cm⁻¹ to 2800 cm⁻¹, 1500 cm⁻¹ to 1400 cm⁻¹ and 900 cm⁻¹ to 700 cm⁻¹ [12]. According to this study, the correlation of 5 isolates showed 99% similarity with reference strain.

After isolation and identification all 5 isolates of *S. thermophilus* were deposited at National Collection of Non-pathogenic Microorganisms of Institute of Microbiology and Biotechnology (CNMN IMB).

The next step of our study was determination of technological properties of the selected strains and their suitability for use as starter cultures. The fermentative activity of lactic bacteria is the most important technological criteria for the appreciation of their use in dairy industry. The intensification of the milk fermentation process and improvement of dairy products quality can be achieved by using biochemically active LAB strains.

The evolution of acidification was monitored for all selected *S. thermophilus* strains, as shown in Figure 2.

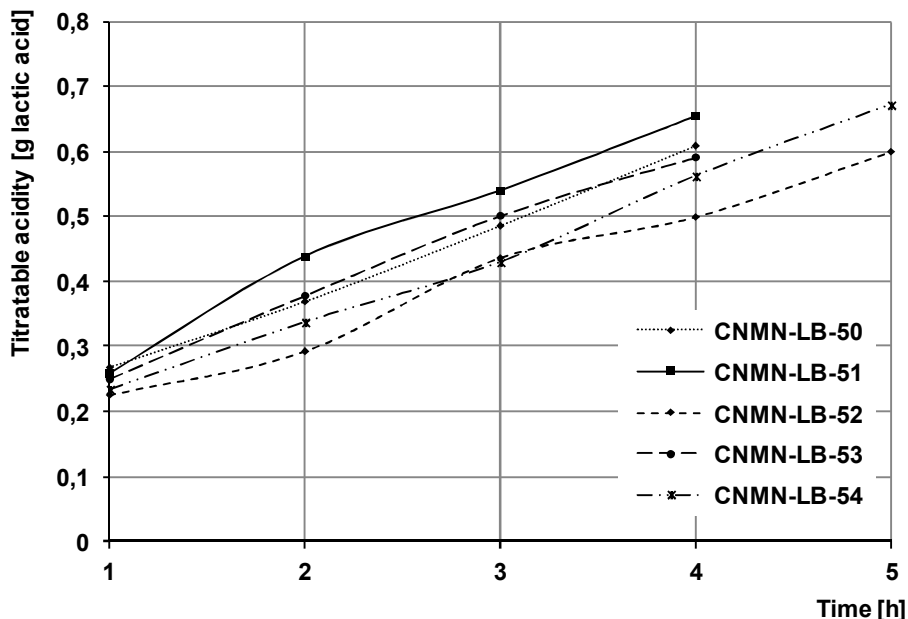


Figure 2. Kinetics of titratable acidity of the *S. thermophilus* strains in milk

Data shows that the selected strains of *S. thermophilus* has a high speed of the milk acidification for 5 hours. The selected strains had a different capacity of lactose fermentation. *S. thermophilus* CNMN-LB-50, CNMN-LB-51, CNMN-LB-53 coagulate skim milk in a 4 ± 0.5 h, *S. thermophilus* CNMN-LB-52 and CNMN-LB-54 in 5 ± 0.5 h.

The strain of *S. thermophilus* along with *Lb. bulgaricus* are used as starter culture for yoghurt production. The main pathogens in the dairy industry are *Escherichia coli*, *Staphylococcus aureus*, *Clostridium botulinum*, *Listeria monocytogenes*. These spoilage bacteria are capable to survive during a production process. *E. coli* and *S. aureus* in dairy products result from post-pasteurization contamination [13]. Therefore, one of the basic parameters for technological interest of LAB selection is their antimicrobial activity. The antimicrobial activity against *E. coli* ATCC 25922 and *S. aureus* ATCC 25923 of 5 selected *S. thermophilus* strains were investigated using the agar-disc diffusion method [14] (table 2).

Table 2
Antagonism of *E. coli* and *S. aureus* by *S. thermophilus* isolates using agar-disc diffusion method

Code of strain	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>
	Zone of inhibition [mm]	
CNMN LB-50	16 \pm 0.5	20 \pm 0.5
CNMN LB-51	18 \pm 0.3	20 \pm 0.3
CNMN LB-52	17 \pm 0.2	19 \pm 0.3
CNMN LB-53	16 \pm 0.2	19 \pm 0.2
CNMN LB-54	17 \pm 0.5	21 \pm 0.5

Based on the results, a total of 5 analyzed strains of *S. thermophilus* showed inhibitor properties against conditional pathogenic bacteria *E. coli* and *S. aureus*. Sterile area varies between 16–18 mm against *E. coli* and 19–21 mm against the *S. aureus*. This indicate the functionally properties of selected strains.

Many thermophilic LAB are capable to produce exopolysaccharide (EPS) that play an essential role in texture forming of fermented products [15]. Therefore EPS producing capacity of selected *S. thermophilus* strains are important technological property. In this study were investigated all five selected strains on ability to EPS production.

As a result of the researches, two strains producing EPS were shown: *S. thermophilus* CNMN-LB-50 $520 \pm 10 \text{ mg} \cdot \text{l}^{-1}$ and *S. thermophilus* CNMN-LB-51 $436 \pm 10 \text{ mg} \cdot \text{l}^{-1}$. In the case of strain *S. thermophilus* CNMN-LB-52, the amount of EPS was low – $24 \pm 5 \text{ mg} \cdot \text{l}^{-1}$. The other 2 strains produce EPS or their amount are very small, and probably co-precipitate with the proteins upon of trichloroacetic acid addition and can no longer be detected after precipitating with ethanol. In general, the EPS yield of strains ranges from $2 \text{ mg} \cdot \text{l}^{-1}$ to $600 \text{ mg} \cdot \text{l}^{-1}$ in milk environment [16–18] and the EPS synthesis capacity is individual for each strain of the same taxonomic group.

On the basis of the obtained results were developed 2 starter cultures for yoghurt production: EPS-producing, non-EPS-producing starter culture, as a control sample served the yoghurt fermented by industrial starter culture (*S. thermophilus* and *L. bulgaricus*). 3 sets of yoghurt were manufactured in the industrial conditions. The results obtained for the yoghurt samples produced using starter cultures with selected *S. thermophilus* strains and industrial curter culture (table 3) showed that the developed starter culture are suitable to be used in yoghurt production.

Table 3

Characteristics of yogurt samples

Parameters	Yoghurt EPS	Yoghurt non-EPS	Yoghurt industrial starter
Fermentation time [h]	4.0±0.1	4.2±0.1	5.0±0.1
LAB cout [log10 CFU·g ⁻¹]	8.8±0.2	8.4±0.3	8.3±0.2
Titrateable acidity [g lactic acid]	0.645±0.01	0.633±0.01	0.626±0.01
EPS [mg·l ⁻¹]	651±10	-	-

Furthermore, developed starter culture possessed the highest fermentation activity comparative with the control sample. The viable count of LAB was at the same level for all samples. No difference was observed between titrateable acidity between samples. In additional, the use of EPS starter culture increase the apparent viscosity that improve the consistency of yoghurt due to microstructure formation where EPS binds free water with the lipid and protein complexes of the product [19, 20].

Conclusion

As a result of the presented research was demonstrated the possibility of isolation from Moldavian raw milk and dairy products of spontaneous fermentation of autochthonous *S. thermophilus* strains with valuable biotechnological properties for industrial application, such as high antibacterial activity and EPS-producing capacity. The five selected strains of *S. thermophilus* showed characteristics adequate for their use as starter culture for yoghurt production. Developed starter cultures characterized by intense acidification of milk 4.0 ± 0.2 h comparative with the industrial starter. The inclusion of EPS *S. thermophilus* strain clearly improved the apparent viscosity of yoghurt.

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Assessment of heavy metal concentration in edible fish muscle and water sample collected from different location in Chittagong: a public health concern

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Abstract

Keywords:

Heavy metal
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Sea
Marine fish
Chittagong

Introduction. The research was carried out to investigate the concentration of heavy metals in fish and water samples collected from different locations of Chittagong District, Bangladesh.

Materials and methods. The concentrations of heavy metals including Cr, Cu, Ni, Pb and Fe in sea water and marine fishes (pama croaker, bombay duck and rat-tail anchovy) were detected by using Air / Acetylene Flame Atomic Absorption Spectrophotometer along Chittagong City areas, Bangladesh.

Results and discussion. The mean concentration of heavy metals were found in water in the range as Cr 0.0138–0.0789 mg/L, Cu 0.0014–0.0284 mg/L, Ni 0.0259–0.2519 mg/L, Pb 0.0109–0.1596 mg/L and Fe 0.2176–1.787 mg/L. The analysis of water samples showed that the distribution of heavy metals in the order of magnitude as Fe > Ni > Pb > Cr > Cu. The variation might be due to location, level of contamination in water through industrial effluents and anthropogenic activities. While the mean concentration of heavy metals were found in all fish samples in the range as Cr 3.2039–16.3495 mg/Kg dry wt., Cu 1.5589–4.5848 mg/Kg dry wt., Ni 0.1101–1.9029 mg/Kg dry wt., Pb 0.4373–2.7638 mg/Kg dry wt. and Fe 30.9599–108.780 mg/Kg dry wt. The distribution of heavy metals in fish samples analyzed were in the order of magnitude as Fe > Cr > Cu > Pb > Ni. The analysis showed that magnitudes of heavy metal were more or less similar with other researchers. The variation might be due to metal accumulation in fish and various fish species living in the same water body but different level of contamination in water. Among all samples, 17% fish samples had excess amount of Cr whereas acceptable limit is 15.0 mg/kg for fish. Mean concentrations of Pb in all fish samples were 17% below detection level, 33% optimum and 33% higher than the maximum permitted concentrations (1.5 mg/Kg). Fe in all fish samples were 33% below, 17% optimum and 50% higher than the maximum permitted concentrations (43 mg/Kg) recommended by FAO/WHO.

Conclusions. Most of the fish species studied are safe to be consumed. Therefore, this study is proposed to draw the attention of health and environmental authorities in need for appropriate regulatory framework.

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Introduction

Fish, as human food, are considered as a good source of protein, polyunsaturated fatty acids (particularly omega-3 fatty acids), calcium, zinc (Zn), and iron [1]. Due to the lower cost and higher nutritive value, it is one of the most important sources among the food products of animal origin [2,3]. In future, seafood will be an vital source of food protein and the safety for human consumption of products from aquaculture is of public health interest [4].

Heavy metals are an important source of food contamination and health hazard. The main threats to human health are associated with exposure to arsenic, cadmium, lead and mercury and copper. Absorption of heavy metals through food has been shown to have serious consequences on health— such as kidney disease, damage to the nervous system, diminished intellectual capacity, heart disease, gastrointestinal diseases, bone fracture, cancer and death [5].

Heavy metals are contaminants in the aquatic environment as well as became toxic health threat for human. Fish play important role in condensing the toxicity of heavy metals which have a great ecological significance due to their cumulative behavior and toxicity [3].

The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal [6,7]. The aim of this study was to assess the levels of some heavy metals in water and fish specimens caught from different localities in Chittagong coastal area, Bangladesh. Public health importance and the hazardous toxic effects of these heavy metals and fish contamination with these were discussed.

Materials and methods

Collection of water samples

The water samples were obtained from 12 sampling stations established along 5 regions (Figure 1). The sampling stations were chosen based on an experimental scheme design following human activities in the area. These regions are main fishing centers of Chittagong, Bangladesh and also, a variety of industries and touristic centers are concentrated in these regions. Following the large volume of population and industries located there, the five regions were selected to measure the heavy metals concentrations in water samples during summer season (Table 1).

Table 1
List of sampling stations for water collection from Chittagong, Bangladesh

Sampling station Code	Regions
W ₁	Majhir Ghat
W ₂	
W ₃	Firingi Bazar
W ₄	
W ₅	Sea-resource Ghat
W ₆	
W ₇	Chaktai Khal
W ₈	
W ₉	Uttar Kattoli
W ₁₀	
W ₁₁	Uttar Kattoli Pond
W ₁₂	

Collection of fish specimens

Pama croaker (*Otolithoides pama*), bombay duck (*Harpadon nehereus*) and rat-tail anchovy (*Coilia ramcarati*) were collected from four different market in Chittagong Metropolitan area, Bangladesh (Table 2). Twenty fish of each species were collected from each market. The fish were washed with deionized water and wrapped separately in acid washed polyethylene bags and were stored frozen at -20°C until analysis.

Materials

All reagents used in this work (HNO₃, NaOH, HCl, KI, HClO₄, K₂CrO₄, NaBH₄, acetylene and argon gas) were of analytical grade and purchased from Merck (Germany).

Table 2

List of market for fish collection in Chittagong, Bangladesh

Location	Fish Samples code		
	Pama croaker	Bombay duck	Rat-tail anchovy
Market 1	P ₁	B ₁	R ₁
Market 2	P ₂	B ₂	R ₂
Market 3	P ₃	B ₃	R ₃
Market 4	P ₄	B ₄	R ₄

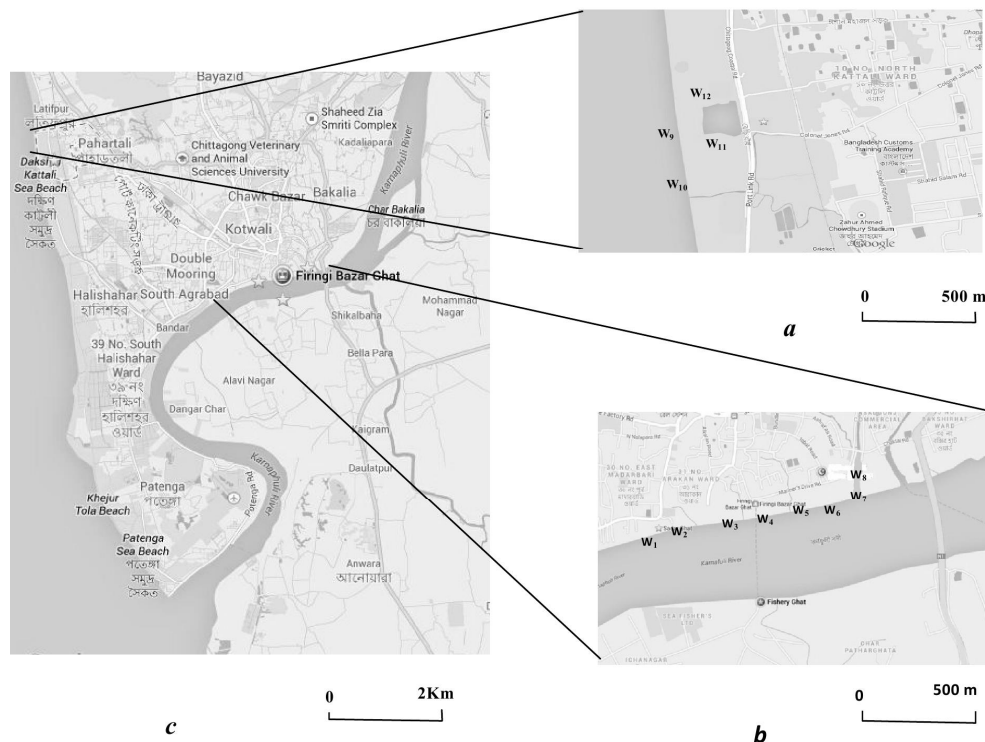


Figure 1. Location map of the study areas (Source: Google map, 2018)

Preparation and analysis of water samples

The water samples were preserved by the addition of 1 ml of concentrated nitric acid per liter until the time of analysis. The analysis of water samples was carried out according to American Public Health Association [8]. They were filtered through 0.45 μ membrane filter. The required volume (100 ml) of the filtrate was used to measure heavy metal levels in water samples by using Air/ Acetylene Flame Atomic Absorption Spectrophotometer.

Preparation and analysis of fish specimens

Fish samples were allowed for thawing and the skin of the fish was removed using a plastic knife to avoid metal contamination. The muscles of fish were taken into pre-acid washed crucibles and they were homogenized separately. The weight of each homogenized sample was recorded. Then the samples were kept in a drying oven at 100° C for more than 24 hrs until a constant weight was observed. The dried samples were then ground into a fine powder using a porcelain mortar and a pestle. Powdered fish tissues were digested using a dry ashing procedure [9]. They were filtered through 0.45 μ membrane filter. The required volume (100 ml) of the filtrate was used to measure heavy metal levels in water samples by using Air/ Acetylene Flame Atomic Absorption Spectrophotometer.

At each step of digestion processes, acid blanks were prepared in order to ensure that the samples and chemicals used were not contaminated. They were analyzed by atomic absorption spectrophotometer. Each set of digestion has its own acid blank and was corrected by using its blank.

Each standard solution was measured 3 times and the mean were plotted. A blank solution of distilled water was used to check accuracy of the standard solutions and it was run after every 10 samples.

The metal content will be calculated using the formula:

$$C = \frac{C_{AAS} \cdot V}{W}$$

where C – concentration (mg Kg⁻¹ or ppm dry wt.)

C_{AAS} – concentration of the element through AAS (ppm)

V – volume made up

Data Analysis

The data obtained from the experiments were statistically analyzed for find out mean and standard deviation among the various samples in triplicate. Data were analyzed using the software, IBM SPSS Statistics, version 20 at the 0.05 level.

Results and dscussion

Heavy metal in sea water

The Mean concentrations and associated standard deviations of Cr, Cu, Ni, Pb and Fe in sea water are presented in Table 3. The mean concentration of heavy metals were found in water in the range as Cr 0.0138–0.0789 mg/L, Cu 0.0014–0.0284 mg/L, Ni 0.0259–0.2519 mg/L, Pb 0.0109–0.1596 mg/L and Fe 0.2176–1.787 mg/L. The distribution of heavy metals in water samples analyzed were in the order of magnitude as Fe > Ni > Pb >

Cr > Cu. Ismail and Saleh (2012) [10] detected heavy metals of water in the order of Fe > Cu, whereas concentrations Pb was below the detection limit. According to El-Kattan (2018) [3], the contents of heavy metals in water were in the order of degree as Cr > Cu > Pb > Fe. Kumar *et al.* (2013) [12] also found heavy metal concentrations in Ennore creek sea water decreased in the order of Cu > Cr > Ni > Pb. The analysis showed that magnitudes of heavy metal were more or less similar with Ismail and Saleh (2012) [10] reported but differ from Ambedkar and Muniyan (2012) [11] and Kumar *et al.* (2013) [12]. The variation might be due to location, level of contamination in water through industrial effluents and anthropogenic activities.

Table 3

Concentration of heavy metal in sea water*

Sampling station Code	Cr (mg/l)	Cu (mg/l)	Ni (mg/l)	Pb (mg/l)	Fe (mg/l)
W ₁	0.0530±0.0034	0.0251±0.0038	0.0259±0.0091	0.1555±0.0130	1.140±0.0340
W ₂	0.0252±0.0234	0.0188±0.0053	0.0384±0.0017	0.1596±0.0204	1.270±0.0586
W ₃	0.0303±0.0244	0.0163±0.0039	0.2350±0.0064	0.0118±0.0013	1.196±0.0387
W ₄	0.0138±0.0123	0.0284±0.0060	0.2519±0.0035	0.0109±0.0054	1.280±0.0206
W ₅	0.0518±0.0173	0.0119±0.0070	0.0568±0.0039	0.1379±0.0141	1.252±0.0179
W ₆	0.0789±0.0197	0.0081±0.0057	0.0815±0.0026	0.1313±0.0241	1.342±0.0431
W ₇	0.0310±0.0060	0.0183±0.0034	0.2007±0.0007	0.0265±0.0039	1.787±0.0088
W ₈	0.0168±0.0058	0.0259±0.0021	0.2024±0.0026	0.0129±0.0060	1.325±0.0063
W ₉	0.0237±0.0096	0.0035±0.0019	0.1179±0.0049	0.1196±0.0117	0.3382±0.0150
W ₁₀	0.0304±0.0230	0.0036±0.0013	0.1348±0.0044	0.1033±0.0190	0.2848±0.0084
W ₁₁	BDL	0.0014±0.0001	0.1770±0.0037	0.0976±0.0049	0.3475±0.0303
W ₁₂	BDL	BDL	0.1998±0.0024	0.0662±0.0336	0.2176±0.0106

* Values are mean ± standard deviation of triplet determinations; BDL=Below Detection Level

The highest concentration level of Cr was found in W₆ (0.0789 mg/L), while the least concentration was detected in W₄ (0.0138 mg/L). But Cr was found below the detection level in pond water. Cu content in W₄ (0.0284mg/L) was higher followed by lowest in W₁₁ (0.0014mg/L). In pond water sample (W₁₂) Cu was analyzed below the detection limit. The highest Ni content was found 0.2519 mg/L in sample W₄ and lowest value 0.0259 mg/L for sample W₁. The maximum concentration of Pd was observed in W₂ (0.1596 mg/L) whereas minimum concentration was observed in W₄ (0.0109 mg/L). The level of Fe was detected highest in sample W₇ (1.787 mg/L) and lowest in W₁₂ (0.2176 mg/L).

Kumar *et al.* (2013) [12] studied on the heavy metal content in sea water and showed that the Cu ranged from 45.29 to 51.02 mg/L, Cr 11.60 to 15.75 mg/L, Ni 12.01 to 15.69 mg/L and Pb 4.10 to 6.20 mg/L. Ambedkar and Muniyan (2012) [11] analyzed Cr, Cu, Pb and Fe content in water. They found 0.70± 0.026 mg/L Cr, 0.50 ±0.025 mg/L Cu, 0.46 ± 0.018 mg/L Pb and 0.32 ± 0.015 mg/L Fe in water. The analysis detected that all water samples were lower Cu, Cr, Ni and Pb content than the range reported by Kumar *et al.* (2013) [12] and Ambedkar and Muniyan (2012) [11] but higher Fe content was found than Ambedkar and Muniyan (2012) [11]. Accumulation of heavy metals in the aquatic environments have been associated with urban runoff, sewage treatment plants, industrial effluents and wastes, mining operations, boating activities, domestic garbage dumps and agricultural fungicide runoff [13].

Heavy metal in sea fish

The Mean concentrations and associated standard deviations of Cr, Cu, Ni, Pb and Fe in sea fish (pama croaker, bombay duck and rat-tail anchovy) are presented in Table 4. The mean concentration of heavy metals were found in all fish samples in the range as Cr 3.2039–16.3495 mg/Kg dry wt., Cu 1.5589–4.5848 mg/Kg dry wt., Ni 0.1101–1.9029 mg/Kg dry wt., Pb 0.4373–2.7638 mg/Kg dry wt. and Fe 30.9599–108.780 mg/Kg dry wt. The distribution of heavy metals in fish samples analyzed were in the order of magnitude as Fe > Cr > Cu > Pb > Ni. Jezierska and Witeska (2006) [14] detected heavy metals in live fish usually follow the ranking: Fe > Pb > Cu > Cd > Hg. According to Ambedkar and Muniyan (2012) [11], the contents of heavy metals in the all fish organs analyzed were in the order of Cr > Cu > Pb > Fe. The analysis showed that magnitudes of heavy metal were more or less similar with Jezierska and Witeska (2006) [14] reported but differ from Ambedkar and Muniyan (2012) [11]. The variation might be due to metal accumulation in fish and various fish species living in the same water body with different level of contamination in water.

Table 4
Concentration of heavy metal in sea water fish*

Fish Sample Code	Cr (mg/Kg dry wt.)	Cu (mg/Kg dry wt.)	Ni (mg/Kg dry wt.)	Pb (mg/Kg dry wt.)	Fe (mg/Kg dry wt.)
P ₁	5.8931±0.4799	2.9826±0.0519	1.2259±0.0201	1.5247±0.1430	34.3399±0.7788
P ₂	3.6049±0.0702	4.0512±0.0246	1.1303±0.0509	1.7494±0.1561	78.4812±0.6901
P ₃	5.7798±0.6082	2.8343±0.0615	1.0733±0.0423	1.5914±0.2352	30.9599±0.6071
P ₄	3.5654±0.4884	4.0548±0.0246	1.1680±0.0588	1.6669±0.1727	79.2792±0.1692
B ₁	3.2039±0.2504	2.8581±0.0246	1.9029±0.0217	1.9964±0.0859	39.0306±0.7464
B ₂	4.1452±0.4207	2.1553±0.0292	0.8601±0.0469	0.5675±0.0489	34.9958±0.2801
B ₃	3.2842±0.3392	2.6436±0.0292	1.7545±0.0491	1.5193±0.2173	37.5378±0.2475
B ₄	4.3846±0.4186	2.1408±0.0604	0.7716±0.0073	0.4373±0.1759	35.079±0.2426
R ₁	16.3495±0.480	4.5848±0.3676	0.9126±0.1773	2.7638±0.3460	108.780±1.778
R ₂	9.7973±0.3718	1.6085±0.1129	0.1101±0.0915	BDL	91.913±4.043
R ₃	16.1246±0.584	4.1436±0.1514	0.5969±0.1071	2.5346±0.8953	106.618±1.289
R ₄	8.1584±0.3056	1.5589±0.3856	0.1459±0.1077	BDL	92.822±0.914

* Values are mean ± standard deviation of triplet determinations; BDL=Below Detection Level

The highest concentration level of Cr was found in P₁ (5.8931 mg/Kg dry wt.), B₄ (4.3846 mg/Kg dry wt.) and R₁ (16.3495 mg/Kg dry wt.) in pama croaker, bombay duck and rat-tail anchovy respectively. Contamination levels of heavy metal in fish are normally compared to the permissible limits recommended by Food and Agriculture Organization (FAO) and World Health Organization (WHO) [15]. In this research, 17% fish samples had excess amount of Cr among all samples whereas acceptable limit is 15.0 mg/kg for fish according to [15,16]. Furthermore, chromium is also more harmful in its lower oxidation state (III). Chromium and chromates are potential carcinogens [17].

The maximum concentration of Cu was observed in P₄ (4.0548 mg/Kg dry wt.), B₁ (2.8581 mg/Kg dry wt.) and R₁ (4.5848 mg/Kg dry wt.) in pama croaker, bombay duck and rat-tail anchovy respectively. Mean concentration of Cu in fish samples was lower compared with FAO/WHO (1984) [15] permissible level (20 mg/Kg). Though copper is an essential element that serves as a cofactor in a number of enzymes systems and necessary for the synthesis of hemoglobin, very high intake of Cu can cause adverse health problems for most living organism [18].

The level of Ni was detected highest in sample P₄ (1.1680 mg/Kg dry wt.), B₁ (1.9029 mg/Kg dry wt.) and R₃ (0.5969 mg/Kg dry wt.) and lowest in P₃ (1.0733 mg/Kg dry wt.), B₄ (0.7716 mg/Kg dry wt.) and R₂ (0.1101 mg/Kg dry wt.) in pama croaker, bombay duck and rat-tail anchovy respectively. According to the FAO/WHO (1984) [15] maximum permissible concentration is 80 mg/Kg for Ni in fish muscle. In this study, Ni concentration for all studied fish species was lower than FAO/WHO standard [15].

Pb content in P₂ (1.7494 mg/Kg dry wt.), B₁ (1.9964 mg/Kg dry wt.) and R₃ (2.5346 mg/Kg dry wt.) were higher in pama croaker, bombay duck and rat-tail anchovy respectively. It was found that mean concentrations of Pb in all fish samples were 17% below detection level (BDL), 17% below, 33% optimum and 33% higher than the maximum permitted concentrations (1.5 mg/Kg) recommended by FAO/WHO [15]. Lead toxicity is known to cause musculo-skeletal, renal, ocular, neurological, immunological, reproductive and developmental effects [11].

The highest Fe content was found in sample P₄ (79.2792 mg/Kg dry wt.), sample B₁ (39.0306 mg/Kg dry wt.) and Sample R₁ (108.780 mg/Kg dry wt.) while the lowest value was found 30.9599 mg/Kg dry wt. in sample P₃, 34.9958 mg/Kg dry wt. in sample B₂ and 91.913 mg/Kg dry wt. in sample R₂ for pama croaker, bombay duck and rat-tail anchovy respectively. It was found that mean concentrations of Fe in all fish samples were 33% below, 17% optimum and 50% higher than the maximum permitted concentrations (43 mg/Kg) recommended by FAO/WHO [15]. Excess amount of iron causes rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness [17].

The presence of heavy metal in the fish sample might be due to untreated industrial discharges, sewage effluents, illegal waste dumping activity, nearby chemical fertilizer industries, domestic wastes and some anthropogenic activities.

Conclusion

Metal has a variety of unpleasant effects, which can impact individual health and produce different harmful changes in human. Knowledge of heavy metal concentrations in sea water and marine fishes are important in order to regulate the consumption of fish. The distribution of heavy metals in water samples analyzed were in the order of magnitude as Fe > Ni > Pb > Cr > Cu. On the other hand, among the metals analyzed in fish muscle, Cr, Pb and Fe were with the highest concentration, while Cu and Ni had the lowest level according to FAO/WHO (1984) [15]. Though the results reveal some higher heavy metal content in fish, it is important to examine the metal concentration in fish through constant monitoring. The metal contaminants perhaps pose little hazard to human for fish consumption. Therefore, future studies should focus on health risks posed by metal contamination in the other biological factor along with seasonal variations.

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Intensification of cooling of tubular blown polymeric packing films with the flowing-down liquid film

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Abstract

Keywords:

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Cooling

Introduction. Analytical and natural researches of process of cooling of a packing film of low density polyethylene (LDPE; high pressure polyethylene) are conducted by the flowing-down water film.

Material and methods. Pilot studies of cooling of the film are conducted at the following parameters: film type – flat; speed of the film – 0.03–0.50 m/s; sizes of the slot-hole distributor of a water film: slot size – 0.4–0.8 mm, slot width – 300 mm; temperature of the cooling water – 15–40 °C. Rational parameters of process of cooling are determined on the basis of mathematical modeling.

Results and discussion. Parameters of a liquid film change only on an entrance zone and depend on liquid concentration, speed of the polymeric tube and initial distribution of speed of the liquid at the exit from a distributive ring. At high values of liquid concentration ($Re > 20000$) only the wall layer of liquid participates in heat exchange.

For the film from LDPE its external surface hardens at distance about 0.01 m from the beginning of contact with water, and an internal surface – at distance about 0.10–0.15 m. Therefore the ring for distribution of liquid needs to be established after the termination of a blowing zone of the polymeric tubular workpiece. It is also necessary to provide the steady movement of a continuous liquid film on an external surface of a polymeric tube on length to 0.2 m from the beginning of contact of liquid from the polymeric film.

Temperature of the cooling water in the range of 20–60 °C significantly does not influence both intensity of cooling process, and physical-mechanical properties of the produced polymeric film.

For thick films from LDPE (thickness more than 200 μm) and over 1 m wide intensity of cooling is limited to the critical liquid concentration.

For practical application of the received results the nomogram for determination of volume liquid concentration of the cooling water, and also volume productivity of the technological line depending on the sizes of a ready tubular blown polymeric film is offered.

Conclusion. The scientific value of results consists in definition of rational conditions of application of liquid cooling of the tubular blown polymeric films produced by extrusion.

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Introduction

Process of cooling of an extruded tubular blown polymeric film significantly influences productivity of the film technological line and quality of the produced product. Due to relative simplicity of constructive and technological realization of process of cooling the air method is the most widespread. However the air method of cooling can not always correspond to high productivity of the basic machine of the film line, namely a screw extruder, especially at production of thick polymeric films [1–4].

It is essential to increase efficiency and intensity of cooling of a polymeric tubular blown polymeric film by means of its interaction with a film of the liquid which is flowing down on its external surface. In this case the method of extrusion of a tubular polymeric film with blowing according to the scheme "from top to down" is the most expedient (unlike air cooling when the scheme "from below up" is the most acceptable).

However for the analysis of efficiency of process of cooling of the tubular blown polymeric film with a gravitational film of liquid it is necessary to investigate hydrodynamics of the liquid film which is flowing down on the moving firm surface and also heat exchange between them.

Literature review and research problems

The main stages of technology influencing quality of tubular blown polymeric packing films are processes of preparation of polymer melt in an extruder, a blowing of workpiece of the polymeric tubular film at the exit from an extruder die, and also cooling of the overblown polymeric tubular film.

The analysis of publications on a problem of production of tubular blown polymeric films showed that the majority of them is devoted to numerical and experimental modeling of separate stages of process of their production. At the same time the main attention is paid to process of preparation of polymer melt in the extruder [5–9], to process of a shaping of a polymer film bubble (the overblown polymer tubular film) [1], and also process of cooling of the formed polymer film bubble with a stream of air [10].

For example, in work [11] production process, and also rheological properties of fusion and tubular blown films of the polypropylene filled with various nanoparticles are in detail considered. At the same time the formed tubular blown film was cooled on air.

The mathematical model of not isothermal process of a shaping of a tubular blown polymeric film is given in work [12]. The analysis of average temperature of a tubular blown film from the low density polyethylene and axial tension arising in it in the course of a blowing is made. Cooling of a film is considered at its contact with air.

In work [13] properties of a tubular blown film from linear low density polyethylene with an additive of hyperbranched polymer are investigated. The produced films differ in high quality of a surface with high operational properties. The studied films were produced by means of a single screw extruder with a diameter of screw of 25 mm and the relation of length of the screw to its diameter 25:1. Cooling of a polymer bubble was carried out by an air stream.

Work [14] investigates properties of a tubular blown packing film from polyvinyl acetate with nanoparticles of starch. The polymeric film was made on a single screw extruder with a diameter of screw of 35 mm; screw long 25 times more of its diameter and extent of compression 1:3. The polymer bubble after its blowing was cooled on air.

Features of traditional technology of a tubular blown polymeric film on the basis of

starch are also considered in works [15, 16].

In work [17] process of blowing and dynamics of further destruction of a biodegradable tubular blown polymeric packing film on the basis of low density polyethylene are considered. Cooling of the film after its blowing it is also carried out on air.

Results of research of process of production of a biodegradable tubular blown film, and also physical-mechanical properties of this film are considered in work [18]. Production of the film in this work is also considered by the method "from below up" with cooling of the film on air. Results of similar researches for a biodegradable tubular blown film on the basis of Polylactic acid are given in work [19].

Results of researches of process of orientation at production of tubular blown films from various types of polyethylene are given in work [20]. Anisotropy of the films produced by an extrusion method with their further cooling on air is also considered. Results of similar researches are given also in work [21].

Possibilities of a blowing of tubular films from polyethylene and polypropylene are considered in work [22].

In work [23] rheological aspects of process of a shaping of a polymer bubble with its further cooling on air are in detail investigated.

Similar problems are also considered in works [24–28].

Works [1, 29] present results of mathematical modeling of process of cooling of tubular polymeric products in a liquid stream. However the models given in these works are not suitable for the analysis of process of cooling with the flowing-down liquid film.

Directly the problem of cooling of polymeric films is considered in work [30]. However these researches concern cooling to a flat polymeric film on the drum which is partially shipped in a water bath. And results of mathematical modeling of process of cooling of a tubular polymeric film by the flowing-down liquid film are given in work [31]. At the same time the analysis only of results of mathematical modeling of the temperature field of epoxy polymeric film is made and stability of the polymer bubble and a liquid film in this work were not considered.

The hydrodynamics and heat exchange of the flowing-down water film at its boiling on a motionless vertical surface are investigated in work [32].

The majority of the settlement dependences of process of heat exchange which are available in literature with participation of the flowing-down film of liquid are suitable for motionless horizontal or vertical surfaces [33] that makes impossible carrying out the analysis of process of film cooling for a mobile vertical surface.

As we see, the majority of researches of the last years concern the analysis of properties of new polymeric compositions and films with their use. At the same time results of researches of process of cooling of a tubular polymeric film with the liquid film which is flowing down on it are practically absent. Therefore researches of process of liquid cooling of hose polymeric packing films is actual.

The objective of the study is the analysis of process of cooling of tubular blown polymeric packing films the flowing-down liquid film. It will allow to determine rational parameters of process of cooling (type of cooling liquid, its temperature and a volume discharge, and also cooling zone length) for cooling of a polymeric film up to the required temperature in a definite time.

It is necessary to solve the following tasks to achieve the objective:

- theoretical investigation the liquid concentration size providing a condition of balance of forces, acting on a polymer bubble at its cooling with the flowing-down liquid film;

- experimentally confirm a possibility of practical realization of process of liquid cooling of tubular blown polymeric films;
- formulate recommendations about rational realization process of cooling of tubular blown polymeric packing films with the flowing-down liquid film.

Materials and methods

Materials

As material of the studied polymeric films low density polyethylene (LDPE) of two types was used:

- LDPE, type 1; density is 919.0 kg/m³; melt flow index of 2 g/10 min at a temperature of 190 °C and load of 21.17 N;
- LDPE, type 2; density is 920.5 kg/m³; melt flow index of 0.3 g/10 min at a temperature of 190 °C and load of 21.17 N.

The studied samples of a polymeric film produced the next way.

The film sample by the sizes 1000×320×0.1 mm (along the polymer bubble) was cut out from the polymer bubble in folded form produced on experimental-industrial working plant. Then the long parties of a sample of the film fixed on a similar film substrate by means of steel wires with a diameter of 0.5 mm. Then the film substrate in horizontal position had on the flat electric heater. In the middle of the made package from one of its short parties between a sample of the film and the film substrate placed jumped to thickness of 0.1 mm thermojunction. After that at a temperature of 180 °C the prototype of the film and the film substrate were welded among themselves. As a result received a monofilm 0.2 mm thick with sealed in its center (on thickness) the thermocouple.

Samples of a polymeric film of other thickness were similarly made.

Experimental installation

Authors developed the experimental stand for research of process of heat exchange at a film current of liquid on a mobile polymeric surface. Also experimental-industrial installation (working plant) was developed for production of a tubular blown polymeric film with liquid cooling on which operating modes of formation of the polymer bubble and a design of the liquid cooling system were fulfilled.

Basic elements of the experimental stand are a head for distribution of the liquid film and the studied flat sample of a polymeric film.

The head is executed in the form of the plane-parallel slot-hole distributor with regulation of distance between sponges (within 0.4...0.8 mm) and slot of 300 mm wide. At the same time as cooling liquid the tap water which is previously purified by means of the filter with a temperature of 15...40 °C was used. Regulation of water temperature was carried out by means of the heat exchanger supplied with resistance electric heaters. The volume flow rate of water was regulated the valve, and measured by the rotameter. Also after each experience carried out control measurement of volume of water by a volume method by means of a measured vessel and a stop watch. Water temperature on an entrance and an exit of the studied sample of the polymeric film was measured by the thermocouples installed in the camera of a distributive head and before a reception funnel.

The prototype of the polymeric film with a film substrate the long parties was fixed on

links of two vertically located infinite chains which covered driving and tension asterisks of the pulling device. At the same time the thermocouple of the film sample was connected to measuring equipment. The run of the film was carried out from the reversible electric motor. The film run in the vertical direction was limited to two limit switches. The working film run – vertical from top to bottom with the regulated speed (0.03–0.50 m/s), and idle run – from below up with a constant speed.

Heating of the polymeric film prototype was carried out thermal radiation from the thermal screen the size 0.3×1,0 m supplied with the flat electric heater of resistance. Temperature of the screen was maintained automatically by means of the device of thermal automatic equipment. For providing the "soft" mode of heating of the sample it was carried out not only regulations of power of the electric heater of the screen, and distance between the screen and the sample.

Steel wires at the edges of the double thickness monofilm during experience played a role of peculiar thresholds, providing at the same time a current of the liquid film, uniform on sample width.

Research was conducted in the following sequence.

By means of chains the sample of the polymeric film is established in extreme top point (at the same time the top limit switch works). After that the necessary mode of heating of epy film with the thermal screen before achievement by a sample of epy polymeric film of necessary temperature was provided.

Then the necessary volume flow rate of water of a certain temperature which at the exit from a head in the form of a flat film flew down on the motionless directing plate established under a sample of the polymeric film and at last got to a reception funnel was provided.

After that the drive of the pulling device was switched on. At the same time chains with the set speed moved the polymeric film sample concerning the distributor of a water film, the sample began to contact to water and was gradually cooled, the lower limit switch of the stand did not work yet. During the movement of the studied sample of a polymeric film the thermogram of its cooling continuously registered.

Thus, at the experimental stand it was possible to conduct numerous researches of cooling process of a certain sample of the polymeric film under various conditions: a volume flow rate of the cooling water, its initial temperature, and also speed of the movement of the sample of the polymeric film.

Experimental-industrial installation for production of the tubular blown polymeric film is developed on the basis of the line for production of a tubular blown film according to the scheme "from above-down". Installation consists of a single screw extruder, an extrusive ring die with the central feeding of melt below which the ring for formation of the water film on an external surface of the polymer bubble is located. For elimination of possible cross fluctuations of the polymer bubble below the liquid distributive ring the stabilizing device with system of the rollers made of a polytetrafluorethylene (teflon) which evenly on a circle contact to the bubble is mounted. Under these device it is mounted the putting and pulling devices executed in the form of two cheeks located at an angle to each other and two rubberized rolls, respectively (Figure 1).

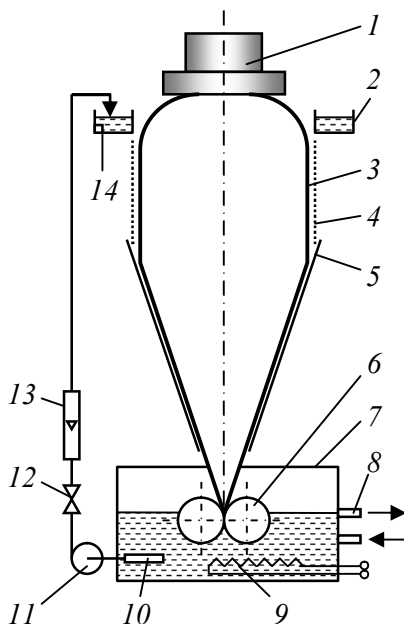


Figure 1. Experimental-industrial installation for production of the tubular blown polymeric film:

1 – extruder ring film die; 2 – the film cooling system with a distributive ring; 3 – tubular blown polymeric film; 4 – film of cooling water; 5 – the putting cheeks; 6 – the pulling rolls; 7 – bathtub for water reception; 8 – drain branch pipe for maintenance of water level in the bathtub; 9 – electrical heater; 10 – filter; 11 – pump; 12 – regulating valve; 13 – rotameter; 14 – resistance thermometer

On the made experimental-industrial installation (working plant) a number of experiments on production of tubular blown films from LDPE in the wide range of values of productivity of the extruder, volume flow rate and reference temperature of the cooling water, and also film thickness depending on conditions of production of the polymeric film was carried out.

Mathematical modeling

Earlier authors developed mathematical model of process of liquid cooling of the tubular blown polymeric film [31]. This model contains the equations of the movement and continuity for the liquid film current by gravity, the equations of conservation of energy for the polymeric film and the liquid film, and also the corresponding initial and boundary conditions on the speed and temperature.

The developed model allows for the set film speed (extruder productivity) and parameters of the film to determine length of a cooling zone or for the set length of a cooling zone to determine the maximum speed of the film with the set parameters.

Results and discussion

Theoretical researches

For determination of design and technological data of cooling process of the tubular blown polymeric film we will consider balance of forces, acting on the polymer bubble limited to two sections: melt exit section from a ring extrusive die and section through contact of the pulling rolls (Figure 2):

$$\vec{F}_0 + \vec{P} + \vec{G} + \vec{P}_w + \vec{F}_r + \vec{F}_{fp} + \vec{F}_{fw} = 0, \quad (1)$$

where \vec{F}_0 is the viscoelastic stretching force operating in the bubble basis (it is result of action of other forces applied to the bubble), N; \vec{P} is force from action of pressure of air inside the bubble, N; \vec{G} is weight of the bubble, N; \vec{P}_w is force of a high-speed pressure of a stream of liquid at the exit from the distributing device of a liquid film, N; \vec{F}_r is bubble stretching force from the pulling rolls, N; \vec{F}_{fp} is bubble friction force on cheeks of the putting device, N; \vec{F}_{fw} is friction force between the polymer bubble and a film of liquid, N.

Let's write down dependence (1) in projections to a longitudinal axis of the bubble

$$F_0 + P - G - P_w \cos \gamma - F_r + F_{fp} - F_{fw} = 0. \quad (2)$$

Now we will consider each of components of dependence (2).

The viscoelastic stretching force operating on the bubble basis

$$F_0 = 2\pi r_0 \delta_0 \sigma_0,$$

where r_0 and δ_0 are initial radius and initial thickness of the polymeric tubular workpiece (initial polymer bubble) at the exit from the extrusive die, respectively, m; σ_0 is the longitudinal tension of stretching in the bubble at the exit from an extrusive die, Pa.

Force from action of pressure of air in the bubble is

$$P = \pi (r_s^2 - r_0^2) \Delta p,$$

where r_s is bubble radius after its blowing, m; Δp – excessive pressure in the bubble, Pa.

The weight of the polymer bubble is equal

$$G = G_1 + G_2 + G_3, \quad (3)$$

where G_1 is weight the bubble on the blowing zone, N; G_2 is weight of the bubble of a cylindrical form on the zone from the place of contact of the bubble with liquid to the zone of folding of the bubble, N; G_3 is bubble weight on the zone from the place of folding of the bubble to the pulling rolls, N.

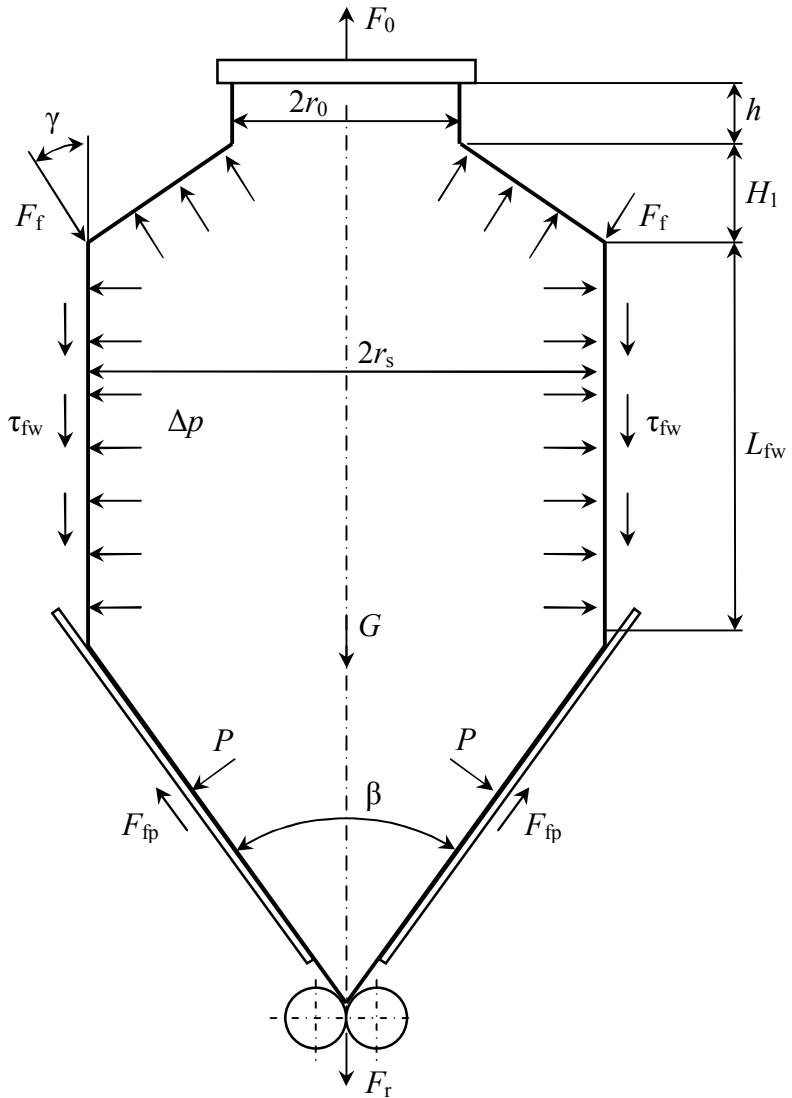


Figure 2. The scheme of forces operating on the polymer bubble at liquid cooling (explanations in the text)

Let's analyze the components of formula (3).

Bubble weight on the blowing zone is [1]

$$G_1 = 2\pi r_0 \delta_0 \rho g \left(\frac{v_0}{v_s - v_0} (H_1 - h) \ln \frac{v_s}{v_0} + h \right), \quad (4)$$

where g is acceleration of gravity, m/s^2 ; v_0 is speed of tubular workpiece at the exit from the extrusive die, m/s ; v_s is speed of the formed bubble at the exit from the blowing zone, m/s ; H_1 is

distance from the beginning of blowing zone prior to contact of the bubble with liquid (the blowing zone), m; h is distance from the extrusive die prior to the beginning of blowing zone, m.

Taking into account practice of production of tubular polymeric films their stability during cooling with the film of liquid is maximum in a case when $h = 0$. Then dependence (4) takes a form

$$G_1 = 2\pi r_0 \delta_0 H_1 \rho g \left(\frac{v_0}{v_s - v_0} \ln \frac{v_s}{v_0} \right). \quad (5)$$

The weight of the cylindrical part of the bubble on the zone from the place of contact of the bubble with liquid to the zone of folding of the bubble

$$G_2 = 2\pi r_s \delta_s \rho g L_{fw}, \quad (6)$$

where δ_s is bubble thickness after its blowing, m; L_{fw} is length of the continuous liquid film flow zone, m.

Bubble weight on the zone from the place of the bubble folding to the pulling rolls

$$G_3 = 2\pi r_s^2 \delta_s \rho g \operatorname{ctg} \frac{\beta}{2}, \quad (7)$$

where β is angle of folding of the polymer bubble.

Taking into account expressions (5)–(7) dependence (3) will equal

$$G = 2\pi r_0 \delta_0 H_1 \rho g \left(\frac{v_0}{v_s - v_0} \ln \frac{v_s}{v_0} \right) + 2\pi r_s \delta_s \rho g \left(L_{fw} + r_s \operatorname{ctg} \frac{\beta}{2} \right).$$

Force of a high-speed pressure of a ring liquid stream

$$P_w = \pi r_s H \rho_w \bar{U}^2,$$

where H is width of slot of the distributive ring of liquid, m; ρ_w is density of liquid, kg/m^3 ; \bar{U} is average speed of liquid in a point of contact with the polymer bubble, m/s.

Friction force between the polymer bubble and the liquid film is

$$F_{fw} = S_{fw} \tau_{fw},$$

where S_{fw} is surface area of the polymer bubble length L_{fw} (from the place of the beginning of contact of the bubble with liquid to the place of a rupture of the continuous ring film of liquid on separate streams), m; τ_{fw} is tangent tension on contact border "polymer – liquid", Pa

$$\tau_{wall} = g \bar{\delta} \rho_w,$$

where $\bar{\delta}$ is average thickness of the liquid film of on the zone of its steady current length L_{fw} , m.

We will determine the average thickness of the liquid film on the zone by length L_{fw} from dependence [34]

$$\bar{\delta} = 0,457 \left(\frac{v_w^2}{g} \right)^{\frac{1}{3}} [\text{Re}(1 \pm \Pi)]^{0,36} \quad \text{if } \text{Re}(1 \pm \Pi) > 1600,$$

where v_w is kinematic viscosity of liquid, m^2/s ; $\Pi = U_0/\bar{U}$ – the simplex considering the relative speed of the liquid film; U_0 is speed of the polymer bubble, m/s ; \bar{U} is average speed of a current of the liquid film on the zone length L_{fw} , which is equal to the average speed of liquid in a point of initial contact with the polymer bubble, m/s .

As the volume fluid flow rate is to constants (losses on evaporation in environment we neglect), taking into account expression for irrigation density $\Gamma_V = \bar{U}H$ the component of a high-speed pressure takes a form

$$P_w = \pi r_s b_w \rho_w \bar{U}^2 \cos \gamma = \frac{\pi r_s \rho_w \Gamma_V^2 \cos \gamma}{H},$$

where b_w is liquid stream width at the beginning of contact with the bubble, m (with an accuracy, sufficient for engineering calculations, it is possible to accept that $b_w = H$).

Bubble friction force on cheeks of the putting device F_{fp} depends on pressure in the bubble, coefficient of friction of polymer on material of cheeks at this temperature and the area of contact of the bubble with cheeks.

In the analysis of dependence (2) practical value has a case when polymer melt is extended not by effort from the pulling rolls, and a body weight and force of a high-speed pressure of the liquid stream F_w .

Let's assume that $F_r = F_{fp}$, then dependence (2) takes a form

$$F_0 + \pi (r_s^2 - r_0^2) \Delta p - G - g \bar{\delta} \rho_w S_{fw} - \pi r_s H \rho_w \bar{U}^2 \cos \gamma = 0. \quad (8)$$

Then taking into account the given dependences expression (8) will have an appearance

$$\begin{aligned} & -g \rho_w S_{fw} \left(\frac{3v_w^2}{4g} \right)^{\frac{1}{3}} \left[\frac{4\Gamma_V}{v_w} \text{Re}(1 + \Pi) \right]^{\frac{1}{3}} - \frac{2\pi r_s \rho_w \Gamma_V^2 \cos \gamma}{H} = \\ & = 0 - g \rho_w S_{fw} \left(\frac{3v_w^2}{4g} \right)^{\frac{1}{3}} \left[\frac{4\Gamma_V}{v_w} \text{Re}(1 + \Pi) \right]^{\frac{1}{3}} - \frac{2\pi r_s \rho_w \Gamma_V^2 \cos \gamma}{H} = 0 \end{aligned} \quad (9)$$

In case of supply of liquid on a normal to a longitudinal axis of the polymer bubble that usually takes place in practice, the component of a high-speed stream of a pressure of liquid becomes equal to zero. Then taking into account that $S_{fw} = 2\pi r_s L_{fw}$ the equation of balance of forces (9) will finally take a form

$$\begin{aligned}
 & -2\pi r_s \delta_s \rho g \left(L_{fw} + r_s \operatorname{ctg} \frac{\beta}{2} \right) - 2\pi r_s g \rho_w L_{fw} \left(\frac{3v_w^2}{4g} \right)^{\frac{1}{3}} \left[\frac{4\Gamma_V}{v_w} \operatorname{Re}(1 + \Pi) \right]^{\frac{1}{3}} = \\
 & = 0 - 2\pi r_s \delta_s \rho g \left(L_{fw} + r_s \operatorname{ctg} \frac{\beta}{2} \right) - 2\pi r_s g \rho_w L_{fw} \left(\frac{3v_w^2}{4g} \right)^{\frac{1}{3}} \left[\frac{4\Gamma_V}{v_w} \operatorname{Re}(1 + \Pi) \right]^{\frac{1}{3}} = 0
 \end{aligned}
 \tag{10}$$

From dependence (10) define the value of volume cooling water concentration Γ_V , satisfying the condition of balance of forces (1) in the process of liquid cooling of the polymer bubble.

From dependence (10) critical values of volume cooling water concentration for tubular films of a different standard size from LDPE were defined. As in the specified dependence unknown sizes are both Γ_V , and L_{fw} , which in turn depends on Γ_V , calculations carried out by method of consecutive approximations.

On critical values of volume cooling water concentration Γ_V counted the volume productivity of the technological line q (or the speed of an exit of polymer melt from the extrusion die v_0) from the condition of achievement of necessary temperature on an internal surface of the polymer bubble.

The nomogram for determination of volume cooling water concentration, and also volume productivity of the technological polymeric film line depending on geometrical parameters of a ready polymer bubble is given in Figure 3.

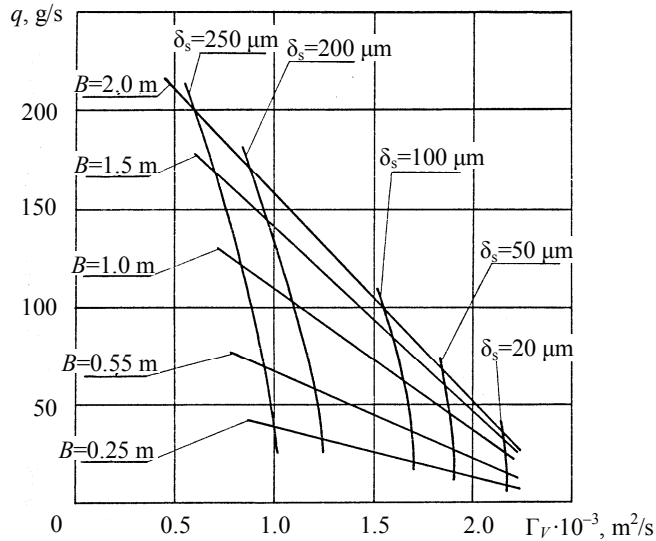


Figure 3. The nomogram for determination of extreme values of volume liquid concentration Γ_V and productivity of the technological line q from the geometrical sizes of the tubular blown polymeric film (film thickness δ_s and width of polymer bubble in folded form B)

As a result of theoretical researches of process of cooling of extruded tubular polymeric films with the flowing-down water film it is established that at the liquid concentration ($\Gamma_V \geq 5.03 \cdot 10^{-3} \text{ m}^2/\text{s}$, or $\operatorname{Re} \geq 20000$) arise essential power load of the polymer bubble. Besides, at such high liquid concentration only the wall layer of liquid

participates in heat exchange that leads to its over-expenditure.

Therefore when carrying out parametrical calculations it is necessary to define critical value of volume liquid concentration which can sustain the polymer bubble of a certain diameter and thickness.

Apparently from nomogram given on Figure 3, the greatest effect of liquid cooling can be reached at production of films with a width of the bubble in folded form to 1 m.

Experimental researches

Parameters of processes of production of tubular blown films of LDPE (types 1 and 2) on experimental-industrial working plant are specified in Table 1.

Table 1
Parameters of processes of production of tubular blown films of LDPE of 1 type and type 2 (in brackets)

Parameter	Unit of measure of physical quantity	Absolute value of physical quantity
Mass productivity of installation	g/s	17.3–69.4 (16.2–68.3)
Speed of the movement of the polymer bubble (stretching speed)	m/s	0.07–0.5
Width of the polymer bubble in folded form	m	0.25; 0.5
Thickness of the polymeric film	mm	0.06–0.2
Melt temperature at the exit from an extrusive die	°C	180
Volume consumption of the cooling water	$10^3 \text{ m}^3/\text{s}$	0.25–0.92
Volume water concentration	$10^3 \text{ m}^2/\text{s}$	0.35–0.88
Initial temperature of the cooling water	°C	20–60
Length of the zone of the continuous current of the liquid film	m	0.15–0.8
Width of the ring slot of water supply	m	0.4–0.8

Follows from table 1 that length of a zone of liquid cooling of the polymer bubble does not exceed 1 m while length of a zone of traditional air cooling of the polymer bubble can reach several meters [1].

Physical-mechanical properties of the tubular blown polymeric film from PEVD, type 2, received at liquid cooling are given in Table 2.

Table 2
Physical-mechanical properties of the tubular blown polymeric film from LDPE, type 2

Sample No	Ultimate strength of the film, MPa		Tensile strain, %		Temperature of the cooling water, °C
	along	across	along	across	
1	20.1	18.9	458	508	20
2	20.6	18.5	432	500	60
3	20.3	18.6	440	512	40
4	19.8	18.1	453	497	50
5	20.9	19.3	439	506	60

Further researches of cooling process of the film were conducted at a temperature of cooling water of 20 °C which corresponds to the average temperature of cold water in a water supply system.

Also influence of a ratio of length of the bubble blowing zone (distance L_{ws} from the extrusive die to the line of contact of cooling liquid with the polymer film bubble) and diameter of the bubble D_s on process of formation of the film on condition of ensuring stability and stability of liquid cooling was investigated.

It is shown that under a condition $L_{ws}/D_s < 0.5$ on the bubble blowing zone has the parabolic form (a convex form), under a condition $0.5 \leq L_{ws}/D_s \leq 1,0$ – conic, and under a condition $L_{ws}/D_s > 1.0$ – the neck is formed (a concave form). At the same time it is proved that the bubble with a parabolic form blowing zone the steadiest, and the films received thus are characterized by a minimum of anisotropy of properties.

Results of researches of physical-mechanical properties of the tubular blowing film at the following data are given in Table 3: diameter – 350 mm, blowing degree – 1.4, the mass productivity of the extruder – 16 g/s (57.6 kg/h). Apparently from tab. 3, length of the blowing zone (or the ratio L_{ws}/D_s) insignificantly influences physical-mechanical properties of the produced film, however, as it was specified, with increase L_{ws}/D_s stability of process of a shaping of the film is broken.

Table 3
Physical-mechanical properties of the film depending on length of a blowing zone

L_{ws}/D_s	Ultimate strength of the film, MPa		Tensile strain, %	
	along	across	along	across
0.343	22.7	22.5	750	775
0.429	22.1	22.0	762	785
0.600	22.8	22.6	770	735
0.857	21.0	22.1	745	780

Results of numerical modeling of process of cooling of the tubular blown polymeric film with the flowing-down film of liquid [31] showed satisfactory compliance to data of experimental researches.

Conclusion

The following conclusions can be drawn, based on the obtained results:

1. Parameters of the liquid film (a speed profile, film thickness) change only on an entrance zone and depend on density of liquid concentration of the polymer bubble and initial distribution of speed of the liquid film at the exit from a distributive ring.
2. At the high values of liquid concentration providing the developed turbulent mode of a current of the liquid film (Reynolds number over 20000), only the wall layer of liquid participates in heat exchange.
3. For the film from LDPE its external surface hardens at distance about 0.01 m from the beginning of contact with water, and an internal surface – at distance about 0.10–0.15 m. Therefore the ring for distribution of liquid needs to be established after the termination of a blowing zone of the polymeric tubular workpiece. It is also necessary to provide the steady movement of a continuous liquid film on an external surface of a polymeric tube on length to 0.2 m from the beginning of contact of liquid from the polymeric film.
4. For thick films from LDPE (thickness more than 200 μm) and over 1 m wide intensity of cooling is limited to the critical liquid concentration.
5. For practical application of the received results the nomogram for determination of volume liquid concentration of the cooling water, and also volume productivity of the technological line depending on the sizes of a ready tubular blown polymeric film is offered.
6. Temperature of the cooling water in the range of 20–60 $^{\circ}\text{C}$ significantly does not influence both intensity of cooling process, and physical-mechanical properties of the produced polymeric film.
7. Extreme values of degree of the polymer bubble blowing ($K_b=2$) and degree of stretching ($K_s=4$) from LDPE are established. It is shown that the limiting stage in production of thin films (thickness of 40 μm and less) with a speed of receiving not less than 0.5 m/s is not process of cooling, and physical-mechanical properties of the film (in particular anisotropy of its properties).

The obtained results of researches allow to determine rational parameters of technological processes of producing tubular blown polymeric films.

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Impact of nanosized aluminum hydroxide on the structural and mechanical properties of sugar beet tissue

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Abstract

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Introduction. The study was conducted to confirm the feasibility of using aluminum hydroxide in the process of extracting sucrose from sugar beet shavings to increase the structural and mechanical properties of beet tissues.

Materials and methods. Investigation of the influence of aqueous solutions of additional reagents on the structural and mechanical properties of beet tissue by the method of hydraulic pressing of samples of sugar beet tissue of cylindrical shape from a geometric dimensional specification. Before that, each of the samples obtained was subjected to heat treatment in aqueous solutions of various reagents at a temperature of 70–72 °C with an experiment duration of 60 minutes.

Results and discussion. Processing of samples of beet tissue with additional solutions of aluminum sulfate, calcium sulfate, aluminum hydroxide and combinations thereof during extraction at a temperature of 70–72 °C will reduce the degree of deformation of samples of beet tissue compared to a sample that has not been treated with additional reagents. The degree of a beet tissue sample treated with a solution of nanosized aluminum hydroxide is 18% lower than the control sample without processing with additional reagents. This result can be explained by the high chemical activity of the aluminum hydroxide reagent. The ions of this compound are capable of forming in the surface layer of tissue fairly stable, insoluble complex compounds with pectin and protein substances, which, adsorbing on a layer of beet tissue, form something similar to the molecular framework, which increases the stability of beet tissue to compressive loads.

The quantity that can accurately describe the quality of beet tissue, its ability to restore its shape and elasticity during periodic compressive loads, is precisely the elastic modulus. During the heat treatment at a temperature of 70–72 °C the elastic modulus of samples of beet tissues, which was subjected to treatment with additional reagents, is 35–40 % higher than a sample of beet tissue without processing with additional reagents.

Conclusions. Application in the process of extraction of nanosized aluminum hydroxide, will ensure the integrity of the structure of beet tissues in the processes of extraction and compression; ensures the high quality of extractant, diffusion and purified juice.

Introduction

The speed and quality of the flow mass exchange processes in the extraction of sucrose from sugar beet shavings most significantly affect the structural and mechanical properties of beet tissue, such as its strength, elasticity and resilience. The traditional diffusion and press method for extracting sucrose from sugar beet shavings with the return of pulp-pressed water for extraction does not always provide the necessary degree of its extraction. The maximal effective extraction of sucrose from sugar beet shavings can be achieved in such a mode of the whole process, when beet tissue have optimal parameters of elasticity and durability. In view of this, today the issues of improving the structural and mechanical properties of sugar beet shavings, namely, the preservation of the integrity of the structure of its tissue in the process of juice extraction are relevant [1–6].

Analysis of scientific research

One of the modern directions of increasing the structural and mechanical characteristics of beet tissues is the use of chemical reagents in the process of extraction [7, 8, 9]. It is known that ions of polyvalent metals (Ca^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} etc.) are able to bind polysaccharides of the cell walls of sugar beet shavings into insoluble complexes, thereby reducing the transition of non-sugars in diffusion juice. Therefore, the use of additional reagents will increase the elastic modulus of sugar beet shavings and, as a result, increase its transport and pressing characteristics.

In today's time, technology has become quite widespread with the use of minced natural gypsum - a sulfate-grade mineral or a slightly dissolved $\text{CaSO}_4\text{-Ca}(\text{HSO}_4)_2$ salt obtained from a sugar plant through oxidation of factory lime milk with sulfur dioxide or sulfuric acid in the process of extraction [10, 11]. But, the given method has a number of problems in application and does not give the desired result, namely - increase of structural and mechanical properties of beet shavings, on which directly the quality parameters of the intermediate products of sugar beet production are directly dependent.

Also, one of the directions of strengthening the beet shaving tissue in the traditional diffusion and press method of extracting sucrose from beet shavings, which has been developing intensively over the last decades, is the chemical effect on beet shavings by appropriate preparation of feed water for the extraction process [12, 13, 14].

The use of additional reagents in the extraction process is essential for the intensification of the sugar beet pulp pressing process by improving its structural and mechanical properties. This problem in our time is extremely relevant due to the increase in prices for fuel materials, which negatively affects the technical and economic indicators of sugar beet pulp drying.

Materials and methods

The maximum effective production of sucrose from beet shavings can be achieved with a diffusion process in which the beetroot tissue has optimal strength and elasticity.

Experimental installation

Investigation of the influence of aqueous solutions of additional reagents on the structural and mechanical properties of beet tissues was carried out on a laboratory installation, presented in Figure 1.

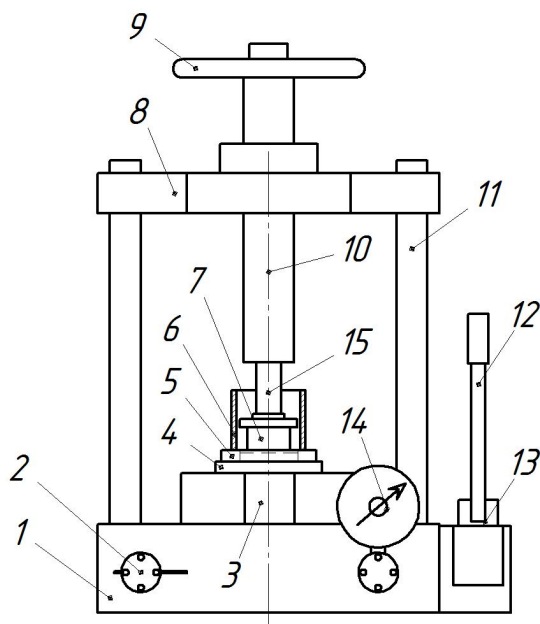


Figure 1. Scheme of an adapted laboratory installation for the study of structural and mechanical characteristics of sugar beet tissue:

1 – housing; 2 – final screw; 3 – tank; 4 – "heel"; 5 – perforated bottom; 6 – removable compression chamber; 7 – prototype; 8 – crossbeam; 9 – screw handle; 10 – clamping screw; 11 – rack; 12 – handle of the pump; 13 – hand pump; 14 – manometer; 15 – hydraulic cylinder.

The principle of hydraulic pressing is based on the installation. The laboratory press (Figure 1) consists of a housing 1, vertical racks 11, to which the crossbeam 8 is attached. On "the heel" 4 is placed a removable compression chamber 6 with a perforated bottom 5. Rotation of the handle of the screw 9 presses the prototype to the pressure screw 10. Using the pump handle 12 pumps oil into the hydraulic cylinder 15 and vertically lifts "the heel" 4. Pressure is controlled by a manometer 14.

The use of this engineering compression equipment provided a high pressure of compaction of the test material to a state with a small (close to zero) volume content of the gas-liquid phase [9].

During pressing, depending on the structural changes taking place in the sample of a disperse material of a given volume, 4 press zones can be conventionally identified (Figure 2).

At the 1st stage of pressing, the dispersion medium (air, water) is displaced from the volume of the material; the process is characterized by a slight increase in pressure with significant movements of the poisson.

At the second stage, the dispersion of the directly dispersed phase takes place; the process is characterized by a reduction in the displacement of the poisson and a gradual increase in pressure.

At the third stage, the gas-liquid phase is displaced from the volume of solid particles of the material; the process is characterized by a significant increase in pressure with small displacements.

At the fourth stage, the components of the dispersed phase (cell destruction) are condensed with a sudden increase in pressure and an insignificant amount of displacement of the poisson.

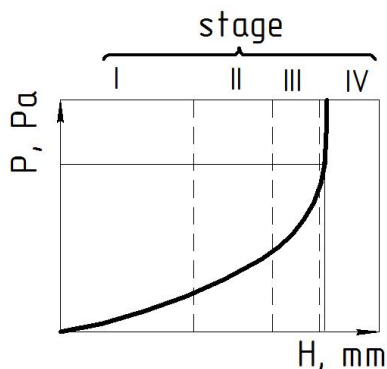


Figure 2. Graph of pressure dependence P on linear deformation H when pressing a disperse test sample

Method

Investigation of the structural and mechanical characteristics of sugar beet tissue was carried out as follows: from the root of sugar beet, samples of cylindrical shape with a diameter of d 50 mm and a thickness (height h) of 25 mm were obtained. Each of the samples obtained was subjected to heat treatment in aqueous solutions of various reagents at a temperature of 70–72 °C with an experiment duration of 60 minutes [15, 21].

Materials

As reagents, solutions of CaSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and nanosized aluminum hydroxide $\text{Al}(\text{OH})_3$ (Fig. 3), obtained by the method of underwater electrospark synthesis [Patent 38461 UA] and a combination of aqueous solutions of these reagents were used. Ratio, reagent concentrations and laboratory results of qualitative indices of diffusion juice are described in Table 1.

Order of research

After the end of the extraction process, the prototypes were placed in the chamber 6 of the laboratory installation and pressings were carried out in the effort range of 0.5–2.5 MPa. At the same time, structural changes and geometric shapes of beet tissue samples, namely, the height h , before and after the compressive loads, were measured. The results were compared with control samples of partially desiccated beetroot tissue [16, 17].

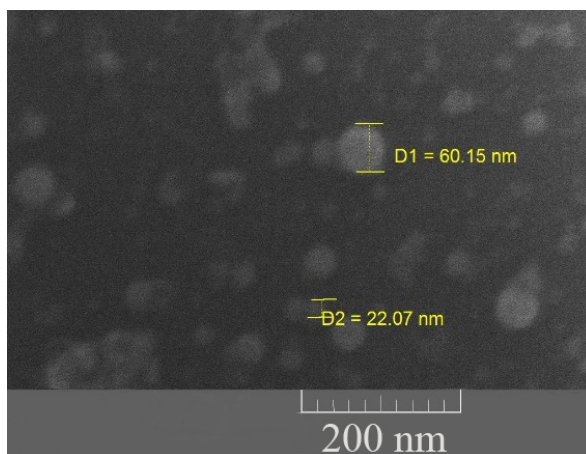


Figure 3. Electron microscopic image of nanosized aluminum hydroxide $\text{Al}(\text{OH})_3$

Processing of research results

The main criterion for determining the degree of quality of beet tissue is its ability to restore its shape and elasticity under periodic compressive loads during extraction and subsequent pressing in production conditions. The magnitude, exactly can describe the quality of the beet tissue, is precisely the elastic modulus [16–20].

The elastic modulus was determined according to Hooke's law with respect to:

$$E = \frac{G}{\varepsilon} \quad (1)$$

where: G – the tension caused in the sample by the acting force; ε – the elastic deformation of the sample caused by stress.

$$G = \frac{P}{F} \quad (2)$$

where: P – the compression force applied to the sample; F – the cross-sectional area of the sample.

$$\varepsilon = \frac{\Delta h}{h} \quad (3)$$

where: Δh – change in the size of the sample after deformation; h – the initial size of the sample to the action of the force.

Results and discussion

The results of the study of the influence of nanosized $\text{Al}(\text{OH})_3$ aluminum hydroxide on the structural and mechanical characteristics of beet pulp are shown in Figure 4 and in Table 1.

Table 1
Impact of aqueous solutions of additional reagents on qualitative indices of diffusion juice and on structural and mechanical characteristics of beet tissue

Method for conducting diffusion of sucrose	Concentrations		Diffusion juice			Effect of purification of diffusion juice, %	The diffusion coefficient, $D \cdot 10^9$	E, MPa		Dry matter of pressed beet pulp, %
	C1	C2	Sugar content, %	Dry matter, %	Purity, %			E1	E2	
Typical	-	-	15,3	16,9	90,53	15,04	0,048	6,1	0,95	23,5
$Al_2(SO_4)_3$	10,0	0,02	15,9	17,3	92,01	29,3	0,077	6,1	0,98	24,2
$CaSO_4$	10,0	0,04	15,4	16,9	91,2	21,45	0,057	6,1	1,12	25,8
$Al(OH)_3$	0,2	0,0015	15,4	16,6	92,9	37,8	0,130	6,1	1,31	27,0
$Al_2(SO_4)_3/$ $CaSO_4$	10,0/ 10,0	0,02/ 0,04	15,6	17,0	91,98	29,02	0,086	6,1	1,31	26,8
$Al_2(SO_4)_3/$ $CaSO_4/$ $Al(OH)_3$	10,0/ 10,0/ 0,2	0,02/ 0,04/ 0,0015	15,9	17,1	93,0	38,73	0,110	6,1	1,35	27,3
$Al_2(SO_4)_3/$ $Al(OH)_3$	10,0/ 0,2	0,02/ 0,0015	16,07	17,3	92,9	37,8	0,101	6,1	1,28	27,2
$CaSO_4/$ $Al(OH)_3$	10,0/ 0,2	0,04/ 0,0015	15,6	16,9	91,8	27,3	0,086	6,1	1,22	26,8

where: C₁ – Concentrations of reagents in solution, %;
 C₂ – Concentrations of reagents to the mass of beet shavings, %;
 E – elastic modulus of sugar beet tissue;
 E₁ – before extraction;
 E₂ – after extraction.

Effect of nanosized aluminum hydroxide on the degree of deformation of sugar beet tissue

Analyzing the diagram of deformation changes (Figure 3), it can be said that the processing of beet tissue samples with additional solutions of $Al_2(SO_4)_2$, $CaSO_4$, $Al(OH)_3$ and their combinations during extraction at a temperature of 70–72 °C will reduce the degree of deformation of the samples beet tissue compared with a sample that has not been treated with additional reagents. In addition, it should be especially noted that the degree of the beet tissue sample that was treated with $Al(OH)_3$ solution is 18% lower than the control sample without treatment with additional reagents (Figure 5). Such an increased stability of beet tissue samples, as well as its rigidity and the ability to resist deformation under the action of force, can be explained by the high chemical activity of the $Al(OH)_3$ reagent [15, 21]. The ions of this compound are capable of forming in the surface layer of the tissue sufficiently stable insoluble complex compounds with pectin and protein substances, which, adsorbed on a layer of beet tissue, form something like a molecular framework that

increases the stability of beet tissue to compressive loads. Describing Figure 5, it is worth mentioning that in sample 5c, there is a part of non-deformable cellular structures of beet tissue in a much larger amount than in sample 5b, which indicates an increase in the stability of beetroot tissue treated with $\text{Al}(\text{OH})_3$ solution and approximation of its elastic characteristics to the tissue sample fresh sugar beet 5a.

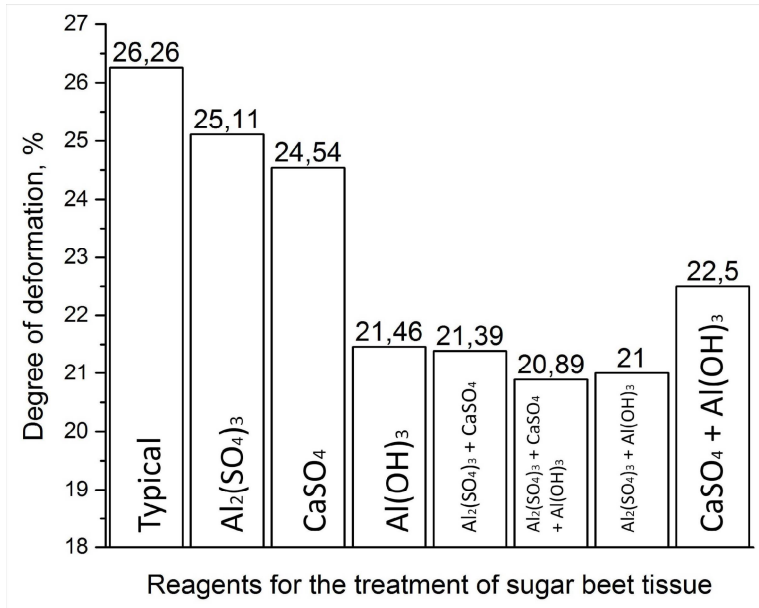


Figure 4. Indicators of deformation changes in samples of beet tissue using different reagents in the sucrose extraction process at a temperature of 70–72 °C

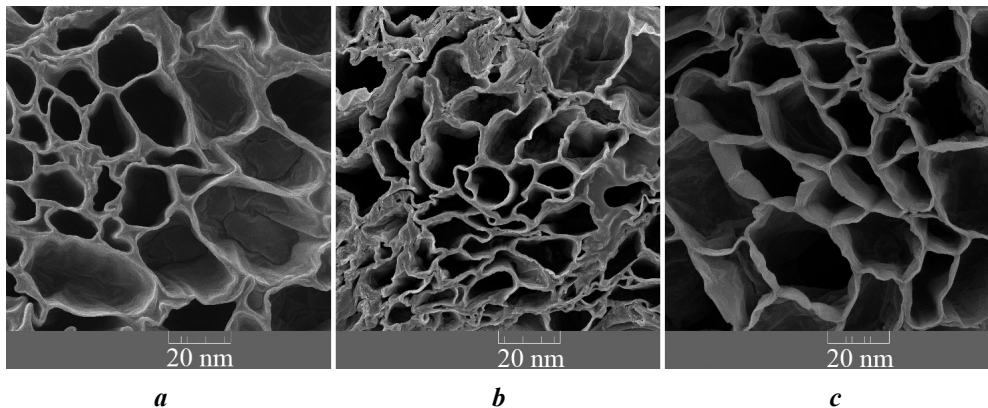


Figure 5. Electron microscopic image of sugar beet tissue samples after compressive loads:
 a - tissue of fresh sugar beet;
 b - sample of sugar beet tissue without finishing with additional reagents in the extraction process;
 c - sample of sugar beet tissue with the addition of reagents, which included $\text{Al}(\text{OH})_3$ during the extraction.

Effect of nanosized aluminum hydroxide on the elastic modulus of sugar beet tissue

The next stage of the work was study the effect of the use of additional reagent solutions in the extraction process on the elastic modulus of sugar beet tissue.

Sugar beet tissue has the ability to partially restore its elasticity when it is water-saturated and at a temperature that causes its thermal denaturation [15, 21]. It is obvious that during the extraction process in batch production plants, the beet shavings absorb moisture and under high temperatures are destroyed. As the temperature of the process increases, high-molecular compounds from less stable tissues pass into solution, the geometry of the sugar beet compounds changes, the hydrodynamic conditions in the diffusion apparatus deteriorate, the permeability of the co-extrusion mixture and, consequently, the purity of the diffusion juice deteriorates [15, 21, 22, 23].

The size of the elastic modulus depends on the turgor of the tissue, which, in turn, depends on the directivity of the functioning of the cell membranes, so the factors that negatively affect the turgor also reduce the elastic modulus. So, for healthy sugar beets, the elastic modulus ranges from 6 to 14 MPa.

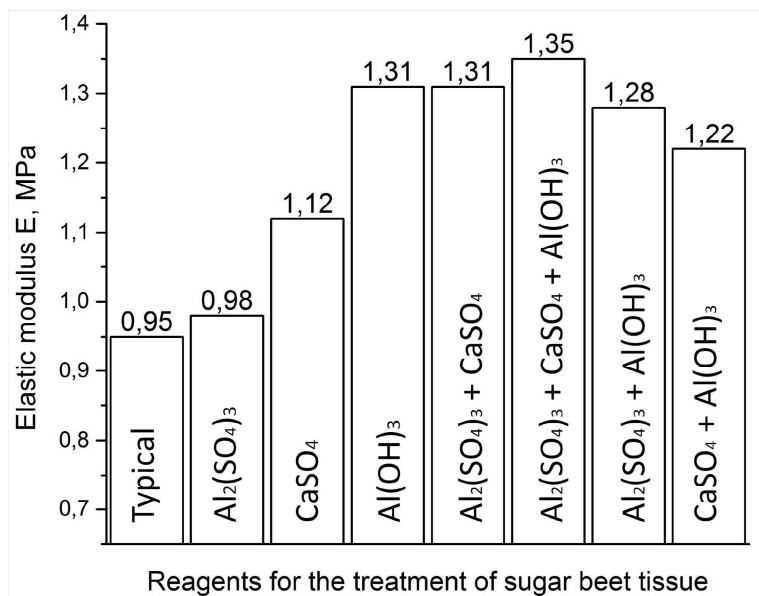


Figure 6. Indicators of the elastic modulus of sugar beet tissue samples when using various reagents in the extraction of sucrose at a temperature of 70–72 °C.

The results of the studies presented in Table 1 were obtained by statistical processing of data from a series of experiments [15, 21]. The accuracy of the measurement results and calculations of the elastic modulus is within 3%, which indicates a fairly high accuracy and reliability of the research results. The advantages of this modified and adapted method for the determination of structural and mechanical characteristics should also include the not

very high complexity of carrying out measurements and calculations, which will allow the fastest control of the elastic characteristics of beet tissue under production conditions.

From the graph of the values of the elastic modulus shown in Figure 6, it follows that during the heat treatment at a temperature of 70–72 °C the elastic modulus of beet samples was treated with additional reagents by 35–40% higher than a sample of beet tissue without finishing with additional reagents. This qualitative difference will ensure the stability of the beet shavings to the external factors and will provide the necessary elasticity in the processes of extraction and subsequent compression under production conditions.

Effect of nanosized aluminum hydroxide on the moisture retention capacity of sugar beet tissue

Based on the results shown in Figure 7, it can be said that, with the same degree of pressing of the beet shavings, more moisture is removed when the additional reagent $\text{Al}(\text{OH})_3$ is used in the extraction process. Therefore, it can be argued that the use of an additional reagent $\text{Al}(\text{OH})_3$ alone or in combination with other reagents in the process of extraction of sucrose from beet shavings allows to achieve a high degree of dehydration of beet pulp that reduces the energy costs for the processes is about further pressing and drying. In addition, such results of water retention capacity indicate that the use of $\text{Al}(\text{OH})_3$ additional reagent in the process of extraction will increase the quantity and quality of pulp-press water, guarantees the production of a reduction in economic costs and improvement of the ecological situation around the sugar plant.

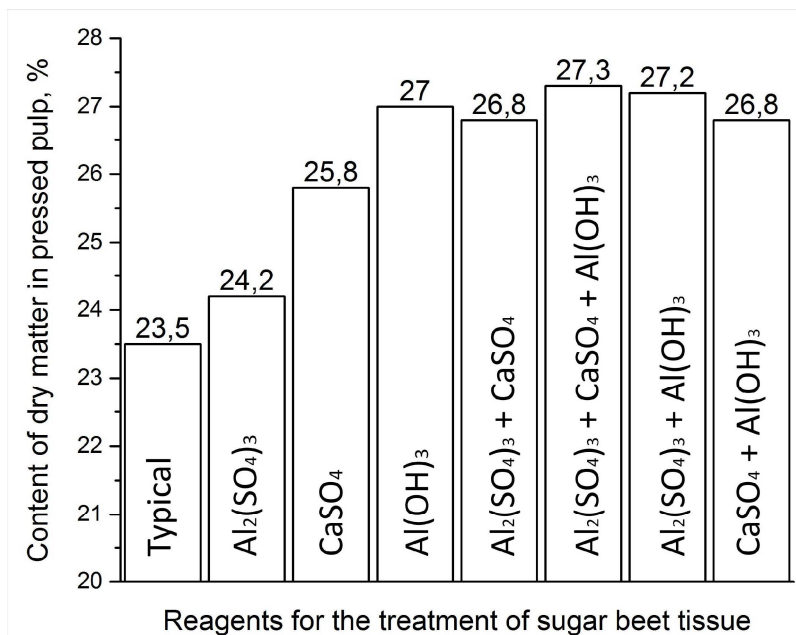


Figure 7. The content of dry substances in samples of sugar beet tissue with the same degree of pressing when using different reagents in the extraction of sucrose at a temperature of 70–72 °C

Conclusions

1. All additional reagents improve the elastic characteristics of the beet tissue, while the nano-sized aluminum hydroxide $\text{Al}(\text{OH})_3$ alone or in combination with other reagents showed that it is its presence in the solution of the additional reagent that guarantees the best structural and mechanical properties of the sugar beet tissue.
2. Application in the process of extraction of nanosized aluminum hydroxide $\text{Al}(\text{OH})_3$, obtained by the method of underwater electrospark synthesis, will ensure the integrity of the structure of sugar beet tissue in the processes of industrial extraction and pressing; guarantees high quality of extractant, diffusion and purified juice.
3. The nanosized aluminum hydroxide $\text{Al}(\text{OH})_3$, in comparison with conventional reagents, is economically and technologically promising for use in the extraction and pressing of sugar beetroot shavings. The use of the proposed method for determining the elastic modulus of a sugar beet sample will allow accurately and promptly control the structural and mechanical characteristics of the raw material during its storage and processing, which allows optimizing the process of extraction of sucrose and compression of the pulp and, thus, improving the yield and quality of the target product.

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Torsional oscillations of an auger multifunctional conveyor's screw working body with consideration of the dynamics of a processed medium continuous flow

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Abstract

Keywords:

Screw
Amplitude
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Introduction. The aim of the article is a mathematical model of vibrations of working part of screw conveyor for transporting friable loads taking into account the changes of closeness of the processed environment, speed of circulation of screw, weight while appearing of the phenomenon of resonance.

Materials and methods. It is researched the turning vibrations of spiral working part of screw multifunctional conveyor, which appear as a result of action of processing environment. The research was carried out by mathematical modelling method.

Results and discussions. The limiting factors which complicate a design are the unevenness of the division of environment along the length of screw; a body makes flexible vibrations; the motion of the processed environment along the working screw causes the small vibrations of bend, causes appearance of “additional forces”. For providing the authenticity of mathematical model it has been introduced the next suppositions: the working part of screw is turned with the permanent angle speed around its longitudinal which in the undeformed position coincides with an axis OX; the transversal transferring of neutral axis of working screw at the arbitrary moment in perpendicular direction of its undeformed position is determined by the vector (in relation to the fixed frame of reference of OXYZ); the continuous stream of processed environment, while its weight changes on unit length slowly along a screw and moves with permanent relative (in relation to working screw) speed.

A mathematical model takes into account the limitation and supposition for the existent screw conveyor with the length of 2,5 and 3 m, which is used for moving the friable loads with the consistence of 10, 20, 40 kg/m. The alternative parameters are the length of the screw, the consistence of the processed environment, the speed of circulation of the screw, weight

On the basis of model the dependences of amplitude of vibrations on the length of screw, consistence of the processed environment, the speed of circulation of the screw, weight are built.

Conclusions. A mathematical model allows to improve the process of development and designing of the screw conveyers of the friable loads providing the reliability of process of transportation and system “the processed environment – the screw working part”.

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Introduction

Presently screw conveyers are the part of complex mechanization and automation of manufacturing. Creation of new and improvement of the existent constructions of screw conveyers with the extended technological possibilities assists to further development of production and increase of their efficiency of the usage. In the modern constructions of cars the usage of screw mechanisms, the nomenclature of which and the specific of exploitation grow constantly; specific weight of these mechanisms in lift-shifting cars according to the different amounts 40...45 % It is established that functional possibilities and technological characteristics of some screw conveyers don't comply the requirements of present time fully according to the signs of expansion of nomenclature of technological processes; results of theoretical and experimental researches, bench equipment etc.. Accordingly the problem of development of the theory and methods of planning of screw conveyers and their descriptions is especially actual has the important value for the economy of the country.

Analysis of the last researches and publications. The conducted analysis of the state of the modern technologies and literary-patent search of constructions of cars and mechanisms for realization of transporting of friable materials [1-3] has showed that in one or another measure they satisfy considerable part of requirements which are pulled out to them, however most constructions of working of working parts of conveyers carry out not only the forward axial moving of material but also implementation of circulating motion, that reduces productivity of such mechanisms. They have a simple construction maximum, differ in compactness and they are reliable in exploitation. At the same time, the substantial disadvantage of screw mechanisms is reduction of their productivity at large frequencies of rotation as a result of increasing of centrifugal forces in the zone of loading that leads to increase of power-hungryness of process of transporting such kinds of devices.

In works [4-8] it was used the method of discrete elements for the analysis of the productivity of screw conveyer including visualization of motion of particles, the angular and axial speed of particles and on the whole twist moment and total force. It is built the model by application of its periodic border for one step of screw and the particle of friable material, it is shown the dependence of the productivity of screw conveyer on operating conditions. It is set that the equability of the stream depends on the construction of screw working part and bunker, form of the particles and the force of the friction to walls. The results of this research can present better the usage of screw feeders for specific materials. In-works [9-13] it was conducted the experiment for determination influence of parameters which have the most influence on horizontal screw conveyers and also power consumption at transporting of grains. So, in works [14] it is adduced the results of researches saving transporting of agricultural materials on the horizontal and aslope located screw working parts, character of motion of stream of material at its loading [15] and overload ing [16], and also moving material by the vertical screws [17] which it is expedient to take into account during realization of researches of moving of stream of root crops and their cleaning.

Experimental and separate theoretical researches of the dynamics of working parts of screw conveyers [18-19], moving of the processed environment along the last items influence on quantitative and on the other occasion and quality descriptions of their vibrations. Thus, influence of dynamics of environment grows with the increasing of the amount of its relative motion toward the screw working part. At the same time the intensive vibrations of screw working part lead to the considerable increase of dynamic tensions, and as a result to reduction of operating term of work of machine. At certain conditions of exploitation of screw conveyers it can take place both the internal and "external

"resonances. Envisaging them is possible only on the base of analysis of decisions of mathematical models which are adequate to dynamic process.

At the same time the questions of the influence of the relative motion of processed environment on the turning vibrations of working part which are important for the assement of work of screw conveyer have not found the proper illustration in literature. For their solution of this task there is a mathematical model of vibrations of working part of screw conveyer for transporting friable loads taking into account the change of consistence of the processed environment, the speed of circulation of screw, mass at appearance of thephenomenon of the resonance.

Materials and methods

Materials

The object of the research is the working part of multifunctional screw conveyer which is used for transporting of friable materials (forage, chemicals, powders, supplements, etc). The subject of the research is turning vibrations of screw working part of screw multifunctional conveyer which arise up as a result of action of processed environment.

Description of the device

The auger compensating multifunctional conveyer is made in the form of a casing 1 with both front 2 and rear 3 supports. Their height can be changed in order to transport materials horizontally and at an angle. The fixed cone trough 4 is firmly fixed to these two supports in several variants – the solid one and with the system of through-holes in its lower part made in a known way. Inside the fixed conical body 4, a conical screw working element 5 with variable steps is installed in the bearing units with the possibility of turning and axial displacement. The bearing bushes 5 are welded to the left 2 and the right 3 supports; in their central openings, the movable cylindrical blocks 6 are set. The bearings are rigidly installed in the middle of blocks; the internal holes of bearing are in contact with the shaft 7 ends of the conical auger 5 with the possibility of axial displacement.

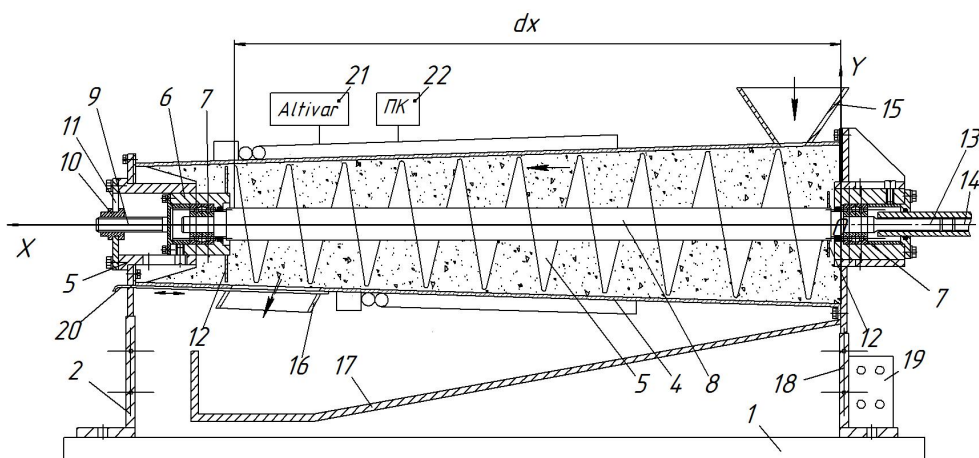


Figure 1. Schematic construction of the auger compensating multifunction conveyor

The ends of movable blocks 6 are covered with lids. A screw 9 is rigidly welded to the left lid 8 of the cylindrical block 6. The screw is in contact with the adjusting nut 10, which is firmly mounted in the axial groove of the lid 11 of the movable cylinder block 6. In addition, the stopper 13 are firmly fixed to the left and right ends of the shaft 7 of the cylindrical movable block 6. They prevent the movement of transport mass beyond the screw working body.

Similarly, at the right end of the screw cone working body, the structure is the same, but the difference is that the ends of the shaft 7 are made with an elongated cut 14, to which the drive shaft 15 of the conveyor is connected. In the loading zone, the boot pipe 16 is installed, and in the unloading zone, the discharge nozzle 17 is installed as well. To fix the screw conical working body 5, in the moving blocks 6, the axial slots 19 are made with screw fixing elements 20. The system is controlled from the console 21.

Results and discussion

Formulation of the problem

In case of the screw working body, the task is considerably complicated: firstly, due to the uneven distribution of the medium along the auger length; secondly, the body performs bending oscillations; thirdly, the movement of the processed medium along the working screw, which carries even small bending oscillations, causes the occurrence of ‘additional forces’, which moments must be factored in the differential equation of torsional oscillations of the system ‘processed environment – screw working body’. Thus, in order to study the torsional oscillations of the screw conveyor working body, a ‘refined’ differential equation of the indicated oscillations should be deduced.

Basic assumptions about the object under study

- The working auger screw rotates with a constant angular velocity Ω around its longitudinal axis, which in the undeformed position coincides with the axis OX ;
- The transverse movement of the neutral axis of the working screw at an arbitrary moment in the direction perpendicular to its undeformed position is determined (with respect to the fixed reference frame of the $OXYZ$) by the vector $\vec{r} = u(x, t)\vec{j} + w(x, t)\vec{k}$;
- A continuous flow of the processed medium, which mass per unit length m slowly varies along the length of the screw ($m = m(x)$) and moves with a constant relative (relative to the working auger screw) velocity V .

Mathematical model solution

A differential equation with partial derivatives is known to be a mathematical model of torsional oscillations of a rectilinear body

$$I \frac{\partial^2 \theta}{\partial t^2} - \frac{\partial}{\partial x} \left(GJ \frac{\partial \theta}{\partial x} \right) = Q \left(\theta, \frac{\partial \theta}{\partial t}, \frac{\partial \theta}{\partial x}, \phi \right) \quad (1)$$

under boundary conditions, which are consistent with the method of body fixation. In Eq. (1) $\theta(x, t)$ - the angle of twisting the elastic body, I - the length moment of inertia relative

to the axis of rotation, G - the shift module, J - the equatorial moment of the cross section, $Q\left(x, \theta, \frac{\partial \theta}{\partial t}, \frac{\partial \theta}{\partial x}, \phi\right)$ - the nonlinear in conjunction with a set of variables $\theta, \frac{\partial \theta}{\partial t}, \frac{\partial \theta}{\partial x}$ periodic by $\phi = \eta t + \phi_0$ function that describes the distribution of external forces moments along the body length relative to the axis of rotation (including the moments of resistance), and η - the frequency of periodic perturbation.

In this case, the inertia force [20] of the conditionally selected element of the screw, the working medium of the length dx and its moment relative to the axis of rotation are determined in accordance with the dependencies

$$\vec{\Phi}_m = 2(m + m_1)\Omega\left(\frac{\partial w}{\partial t}\vec{j} - \frac{\partial u}{\partial t}\vec{k}\right)dx \quad (2)$$

$$M_m^\phi \vec{i} = (u\vec{j} + w\vec{k}) \times \vec{\Phi}_m = -2(m + m_1)\Omega\left(u\frac{\partial u}{\partial t} + w\frac{\partial w}{\partial t}\right)\vec{i}dx, \quad (3)$$

where $m_1 = m_1(x)$ - the mass per unit length of the auger conveyor crew.

Similarly, the inertia force of the processed medium and its moment relative to the axis of rotation is defined, taking into account the medium motion along the deformed screw

$$\vec{\Phi}_{cep} = 2m\Omega V\left(\frac{\partial w}{\partial x}\vec{j} - \frac{\partial u}{\partial x}\vec{k}\right)dx. \quad (4)$$

$$M_{cep}^\phi \vec{i} = (u\vec{j} + w\vec{k}) \times \vec{\Phi}_{cep} = -2m\Omega V\left(u\frac{\partial u}{\partial x} + w\frac{\partial w}{\partial x}\right)\vec{i}dx. \quad (5)$$

Other inertia forces of the processed medium continuous flow are not considered. The moment of the forces relative to the rotational axis of the working screw is zero and therefore does not affect its torsional oscillations. The above allows presenting a refined differential equation of torsional oscillations of the system 'processed medium continuous flow - screw working body'

$$\frac{\partial^2 \theta}{\partial t^2} - \frac{GJ_0}{I_0} \frac{\partial^2 \theta}{\partial x^2} = \frac{1}{I_0} f\left(x, \theta, \frac{\partial \theta}{\partial t}, \frac{\partial \theta}{\partial x}, \phi\right) \quad (6)$$

$$\frac{GJ_0}{I_0} = \frac{G}{\rho}$$

where:

$$f\left(x, \theta, \frac{\partial \theta}{\partial t}, \frac{\partial \theta}{\partial x}, \phi\right) = Q\left(x, \theta, \frac{\partial \theta}{\partial t}, \frac{\partial \theta}{\partial x}, \phi\right) - 2\Omega\left[(m + m_1)\left(u\frac{\partial u}{\partial t} + w\frac{\partial w}{\partial t}\right) + mV\left(u\frac{\partial u}{\partial x} + w\frac{\partial w}{\partial x}\right)\right]$$

G - the shift module, I_0 - the length moment of the inertia relative to the axis of a working screw together with the processed medium, J_0 - the equatorial moment of the working screw cross-section and the values below are considered constant.

Further calculations relate to the development and study of the differential equation solution (6) under boundary conditions

$$\theta(x, t)|_{x=0} = \theta(x, t)|_{x=l} = 0 \quad (7)$$

which correspond to the twisting oscillations of the auger working body with free ends, and l - the distance between the bearings, in which it rotates. Based on the following physically grounded statements, the boundary problem Eq. (6), Eq. (7) can be solved:

1. The maximum value of the right-hand side of differential equation Eq. (6) is a small value in comparison with the maximum value of the 'restoring moment of torsion', that is, the second summand of its left-hand side;

2. Functions of the deflection $u(x, t)$, $w(x, t)$ of the screw working body are determined [21] by a wave form with an amplitude a , a wave number $\lambda_k = \frac{k\pi}{l}$, a

frequency $\omega_k = \sqrt{\left(\frac{k\pi}{l}\right)^4 \frac{E\bar{I}_0}{m+m_1} - \Omega^2}$, \bar{I}_0 - the inertia moment of the working screw cross-

section relative to the neutral axis of the cross-section, which is perpendicular to the plane of oscillation. In this case, the right-hand side of differential equation Eq. (6) can be presented in the form

$$f(x, \theta, \dots, \phi) = Q(x, \theta, \dots, \phi) - 4\Omega a^2 \left(2(m+m_1)\omega_k \sin^2 \lambda_k x \sin 2\psi_k + mV\lambda_k \sin 2\lambda_k x \cos 2\psi_k \right), \psi_k = \omega_k t + \psi_0 \quad (8)$$

where ψ_0 - a constant. Thus, the problem solution was reduced to developing a solution of differential Eq. (6), considering Eq. (8) under boundary conditions Eq. (7).

The most effective methods of studying 'weakly nonlinear' oscillatory systems with lumped masses or distributed parameters are methods based on the main idea of perturbation methods [22-25]. In relation to the considered problem, the application of the principle of one-frequency oscillations and the basic idea of the Bubnov Galerkin method [21, 29-30] allow reducing the boundary problem Eq. (6), Eq. (7) to integration of the system of ordinary quasilinear differential equations

$$\ddot{T}_1(t) + \left(\frac{\pi}{l}\right)^2 \frac{GJ_0}{I_0} T_1 = \frac{1}{I_0} \left\{ \int_0^l Q\left(x, T_1 \sin \frac{\pi}{l} x, \dots, \phi\right) \sin \frac{\pi}{l} x dx - \frac{16l}{3\sqrt{\pi}} \Omega a^2 (m+m_1) \omega_1 \sin 2\psi \right\} \quad (9)$$

$$T_2(t) + \left(\frac{2\pi}{l}\right)^2 \frac{GJ_0}{I_0} T_2 = \frac{1}{I_0} \left\{ \int_0^l Q\left(x, T_2 \sin \frac{2\pi}{l} x, \dots, \phi\right) \sin \frac{2\pi}{l} x dx - 4\Omega a^2 l m V \cos 2\psi \right\} \quad (10)$$

Based on dependences Eq. (9), Eq. (10), the most interesting cases of torsional oscillations from the theoretical and practical point of view are cases:

$$\begin{aligned} \text{a. } \frac{\pi}{l} \sqrt{\frac{GJ_0}{I_0}} &\approx \sqrt{\left(\frac{2\pi}{l}\right)^4 \frac{E\bar{I}_0}{m+m_1} - \Omega^2}, & \text{b. } \frac{2\pi}{l} \sqrt{\frac{GJ_0}{I_0}} &\approx \sqrt{\left(\frac{2\pi}{l}\right)^4 \frac{E\bar{I}_0}{m+m_1} - \Omega^2}, \\ \text{c. } \frac{k\pi}{l} \sqrt{\frac{GJ_0}{I_0}} &\approx \eta. \end{aligned}$$

These cases are called resonant. The case (c) is defined by external factors, then, the cases (a) and (b) – by bending oscillations of the working screw. In addition, the case (a) considers purely bending oscillations and rotations of the working screw, then, the case (b) – the processed medium additional motion along the working screw, more precisely, the moment relative to the rotation axis of the Coriolis force of the inertia of the processed medium.

Mathematical model discussion

According to individual studies [26-28], combination resonances of higher orders are less important than the above-mentioned ones;

The methods of studying the resonance phenomena on different frequencies do not fundamentally differ. Therefore, the general statements based on the generalization of the main idea of the Van der Pol method to the differential equation Eq. (9) or Eq. (10) are presented.

Thus, the resonance oscillations under the conditions a), b), c) are described by the dependence $T_i(t) = \bar{a}_i(t) \cos(\bar{\omega}_i t + \vartheta_i(t))$, where $\bar{\omega}_i$ is one of the frequencies, on which resonance oscillations are considered, and the parameters $\bar{a}_i(t)$ and $\vartheta_i(t)$ (the amplitude and phase difference of resonant oscillations) are determined by the differential equations:

a. For the resonance at the first angular rotation velocity of the screw working body

$$\begin{aligned} \frac{da_1}{dt} = & \frac{1}{2\pi^2 \bar{\omega}_1 I_0} \int_0^l \int_0^{2\pi} \int_0^{2\pi} Q \left(x, \bar{a}_1 \sin \frac{\pi}{l} x \cos \psi, \dots, \phi \right) \sin \frac{\pi}{l} x \sin \phi dx d\psi d\phi - \\ & - \frac{16l}{3\bar{\omega}_1 I_0} \Omega_1 a^2 (m + m_1) \omega_1 \cos \gamma_1, \\ \frac{d\gamma_1}{dt} = & \frac{\pi}{l} \sqrt{\frac{GJ_0}{I_0}} - \sqrt{\left(\frac{2\pi}{l}\right)^4 \frac{EI_0}{m + m_1} - \Omega_1^2} + \\ + & \frac{1}{2\pi^2 \bar{\omega}_1 \bar{a}_1 I_0} \int_0^l \int_0^{2\pi} \int_0^{2\pi} Q \left(x, \bar{a}_2 \sin \frac{\pi}{l} x \cos \psi, \dots, \phi \right) \sin \frac{\pi}{l} x \cos \phi dx d\psi d\phi + \frac{16l}{3\bar{\omega}_1 \bar{a}_1 I_0} \Omega_1 a^2 (m + m_1) \omega_1 \sin \gamma_1; \end{aligned} \tag{11}$$

b. For the resonance at the second angular rotation velocity of the screw working body

$$\begin{aligned} \frac{da_2}{dt} = & \frac{1}{2\pi^2 \bar{\omega}_2 I_0} \int_0^l \int_0^{2\pi} \int_0^{2\pi} Q \left(x, a_1 \sin \frac{2\pi}{l} x \cos \psi, \dots, \phi \right) \sin \frac{2\pi}{l} x \sin \phi dx d\psi d\phi + \\ & + \frac{2\Omega_2 a^2 V l m \pi}{\bar{\omega}_2 I_0} \sin \gamma_2, \\ \frac{d\gamma_2}{dt} = & \frac{2\pi}{l} \sqrt{\frac{GJ_0}{I_0}} - \sqrt{\left(\frac{2\pi}{l}\right)^4 \frac{EI_0}{m + m_1} - \Omega_2^2} + \\ + & \frac{1}{2\pi^2 \bar{\omega}_2 \bar{a}_2 I_0} \int_0^l \int_0^{2\pi} \int_0^{2\pi} Q \left(x, a_2 \sin \frac{\pi}{l} x \cos \psi, \dots, \phi \right) \sin \frac{\pi}{l} x \cos \phi dx d\psi d\phi - \frac{2\Omega_2 a^2 V l m \pi}{\bar{\omega}_2 \bar{a}_2 I_0} \cos \gamma_2; \end{aligned} \tag{12}$$

c. For the resonance on the frequency of the external periodic perturbation

$$\frac{d\bar{a}_3}{dt} = \frac{1}{2\pi l \mu I_0} \int_0^l \int_0^{2\pi} Q \left(x, \bar{a}_3 \sin \frac{\pi}{l} x \cos(\gamma_3 + \varphi), \dots, \varphi \right) \sin(\gamma_3 + \varphi) \sin \frac{\pi}{l} x dx d\varphi \quad (13)$$

$$\frac{d\gamma_3}{dt} = \frac{\pi}{l} \sqrt{\frac{GJ_0}{I_0}} - \mu + \frac{1}{2\pi l \bar{\omega}_1 I_0 \bar{a}_3} \int_0^l \int_0^{2\pi} Q \left(x, \bar{a}_3 \sin \frac{\pi}{l} x \cos(\gamma_3 + \varphi), \dots, \varphi \right) \cos(\gamma_3 + \varphi) \sin \frac{\pi}{l} x dx d\varphi,$$

where $\bar{\omega}_1 = \frac{\pi}{l} \sqrt{\frac{GJ_0}{I_0}}$, $\bar{\omega}_2 = \frac{2\pi}{l} \sqrt{\frac{GJ_0}{I_0}}$.

Consequently, the internal resonances occur only due to a certain correlation between the frequency of the own transverse and torsional oscillations, more precisely, due to the distribution of masses in the system ‘processed medium - auger working body’, its geometrical dimensions and the angular velocity of the working screw. According to equations Eq. (11) and Eq. (12), in Figure 1 and Figure 2, under the condition

$$Q = Q \left(x, \theta, \frac{\partial \theta}{\partial x}, \frac{\partial \theta}{\partial t}, \phi \right) = \delta \left(\frac{\partial \theta}{\partial t} \right)^s \quad (\delta, s - \text{steels}),$$

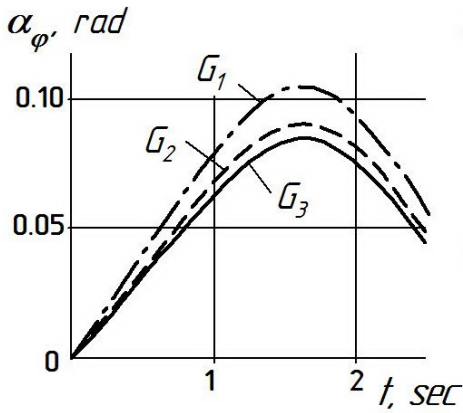
the amplitudes of torsional oscillations of the working screw during the transition through the resonance are presented for different lengths of the working screw, and different values of its densities (see figure 1), and different values of masses per unit length of the processed medium and its velocity (see Figure 2).

On the basis of theoretical data it is shown the results of experimental researches of dependence of the productivity of the inclined ickyu conveyer from the internal diameter of casing of D , epy angle of slope of conveyer γ and frequency of rotation of working part n during the transporting of friable material (wheats). It is deduced the equation of regression for determination the productivity of transportation of wheat.

During transportation of wheat :

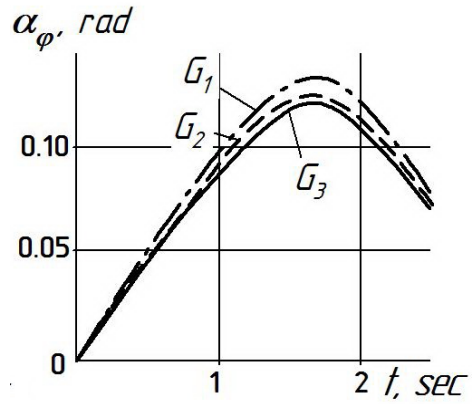
$$Q_{(D,\gamma,n)} = 3,387 - 117,52D + 2,49 \cdot 10^{-2} \gamma - 8,92 \cdot 10^{-3} n - 0,328D\gamma + +0,234Dn - 3,4 \cdot 10^{-5} \gamma n + 880D^2 \quad (14)$$

On the basis of the experimental researches it was set the maximal value of the productivity – 6,4 t/hour, and minimum – 0,2 t/hour. The basic factors which influence on increasing the productivity are the external diameter of screw working part and amount of turns and at the increase of angle of slope of conveyer the productivity is reducing.



a

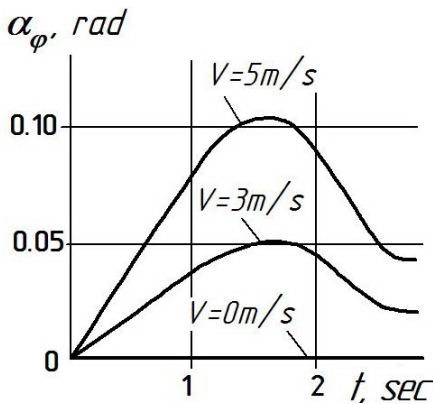
$m = m_1 = 10 \text{ kg/m}$, $E = 2 \cdot 10^{11} \text{ MN/m}^2$,
 $\bar{I}_0 = 2.78 \cdot 10^{-7} \text{ m}^4$, $G_1 = 1.6 \cdot 10^{11} \text{ MN/m}^2$,
 $G_2 = 1.4 \cdot 10^{11} \text{ MN/m}^2$, $G_3 = 1.3 \cdot 10^{11}$
 MN/m^2 , $l = 3 \text{ m}$



b

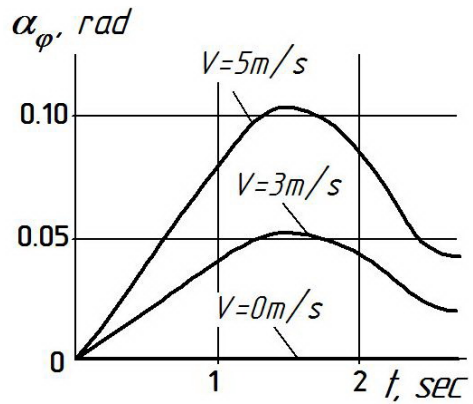
$m = m_1 = 10 \text{ kg/m}$, $E = 2 \cdot 10^{11} \text{ MN/m}^2$,
 $\bar{I}_0 = 2.78 \cdot 10^{-7} \text{ m}^4$, $G_1 = 1.6 \cdot 10^{11} \text{ MN/m}^2$,
 $G_2 = 1.4 \cdot 10^{11} \text{ MN/m}^2$, $G_3 = 1.3 \cdot 10^{11}$
 MN/m^2 , $l = 2.5 \text{ m}$

Figure 2. Change in the amplitude of torsional oscillations of the working screw during the transition through the resonance on the first frequency of transverse oscillations under the following values of parameters



a

$m = 40 \text{ kg/m}$, $m_1 = 10 \text{ kg/m}$, $E = 2 \cdot 10^{11}$
 MN/m^2 , $\bar{I}_0 = 2.78 \cdot 10^{-7} \text{ m}^4$, $G_1 = 1.3 \cdot 10^{11}$
 MN/m^2 , $l = 3 \text{ m}$



b

$m = 20 \text{ kg/m}$, $m_1 = 10 \text{ kg/m}$, $E = 2 \cdot 10^{11}$
 MN/m^2 , $\bar{I}_0 = 2.78 \cdot 10^{-7} \text{ m}^4$, $G_1 = 1.3 \cdot 10^{11}$
 MN/m^2 , $l = 3 \text{ m}$

Figure 3. Change in the amplitude of torsional oscillations of the working screw during the transition through the resonance on the second frequency of transverse oscillations under the following values of parameters

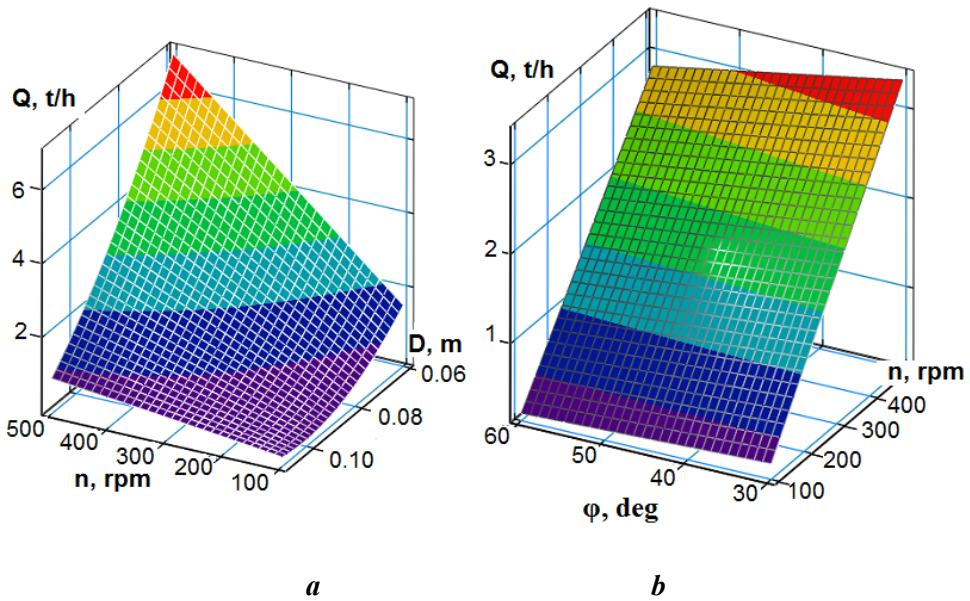


Figure 4. Surface of review of the change of the productivity of conveyer Q during transportation as a functional:

$$\text{a} - Q = f_{(Q)}(D; n); \quad \text{b} - Q = f_{(Q)}(n; \gamma)$$

Conclusions

Based on the developed method of studying the torsional oscillations of the screw working auger conveyor with consideration of its transverse oscillations and the motion of the processed medium continuous flow, the following conclusions are made:

1. The constant angular rotation velocity of the screw working body decelerates the frequency of the own bending oscillations of the screw working body;
2. Relative movement of the processed medium along the screw working body, which rotates and performs transverse oscillations, acts additionally on the body as the periodic torque;
3. According to the above-mentioned, the resonances can occur during the torsional oscillations of the screw working body on the first fundamental and the second frequencies of the twisting oscillations of the working body and on the frequency of external periodic perturbation;
4. The amplitude of the transition through the resonance on the fundamental frequency of bending oscillations assumes smaller value for screw working bodies with greater torsional rigidity;
5. The amplitude of torsional oscillations during the transition through the resonance on the second fundamental frequency is higher due to the larger values of the quantity of processed medium relative motion;

6. The amplitude of torsional oscillations during the ‘fast’ transition through the resonance on the frequency of external or internal perturbations is smaller than during the ‘slow’ one.

The obtained results can serve as a basis for choosing the basic technological and operational parameters of a screw multifunctional conveyor. The results reliability is confirmed by obtaining in the limiting case under $V \rightarrow 0$ the known [3], which relate to the influence of bending oscillations of the elastic screw on the torsional ones, without considering the motion of the processed medium.

The results of modeling correlate (call) with the results of researches [1, 8, 15, 21, 29]. The received results should be followed for further planning the similar screw conveyers with similar changeable parameters.

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Effective robust optimal control system for a lamellar pasteurization-cooling unit under the conditions of intense external perturbations

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Abstract

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Introduction. Investigated robust optimal control system of pasteurization-cooling unit, functioning under conditions of intensive external disturbances, information and structural uncertainty in order to improve the efficiency.

Materials and methods. Methods of system analysis, mathematical statistics and identification used to construct a mathematical model of the control object. For the synthesis of the robust optimal controller, the 2-Riccati approach H₂ control problems is applied, and to reduce the order of the received regulator – method for balanced model reduction.

Results and discussion. The work of the pasteurization unit is considered, since it is a key component of dairy production. Since the results of the operation of traditional automated systems depend on the intensity and quality of information flows, microprocessor technology, algorithmic and software, it is proposed to supplement them with robust optimal controllers based on the 2-Riccati approach. Identified a mathematical model of the object, which consists of linear differential equations of the seventh order, it is possible to synthesize a robust optimal controller of the 6th order. Performance indicators are calculated by comparing the synthesized system and the system with local regulators. In a robust optimal system, the magnitude of uncertainty increased fourfold, and the dispersion of control signals decreased fourfold, which proves its energy efficiency.

Conclusion. The performed modeling and calculation of qualitative characteristics showed a significant advantage of the synthesized system in front of systems with local regulators.

Introduction

During Industry 4.0, when industrial enterprises grow into Smart Factory, combine advanced production technologies, automated production, communications and information technologies, the issue of improving automated control systems of technological processes based on intelligent approaches is relevant [1, 25]. However, in terms of automation, such managing facilities have common problems of mismatch in temperature and quality values, uneven consumption and temperature of the incoming flow, as well as other internal and external factors which negatively affect the quality of the output product and the energy efficiency of the whole system. All these factors can be described in the uncertainty range of the object, and then it is possible to construct a robust optimal control system under one correctly selected criterion [2–5].

For production objects with significant uncertainties of the use of H_2 - or H_∞ -norms of the Hardy space of the closed system transfer function as a control criterion are effective for the proper types of input and output signals, whereby the system obtains the property of low-sensitivity (robustness) towards internal and external object changes [6]. The control device thus synthesized has a high order, and as a result, the complexity of the software implementation.

Since the object of study works under conditions of parametric and structural uncertainty, as well as under the influence of intense external disturbances, the goal of the work is to increase the efficiency of its control system by synthesizing an effective control device based on robust optimal practices.

Materials and methods

According to the purpose of the article, the following approaches and methods were used: system approach, statistical analysis, parametric identification of dynamic mathematical models, synthesis of the H_2 -regulator in the 2-Riccati approach, reduction of mathematical models, mathematical modeling. Using the system approach [7, 8], the theoretical bases of the study, in particular, the orderly and structure of the model of the control object are well-documented. The statistical analysis of process variables substantiated the essence of uncertainties, and also helped shape the form of weight transfer functions for external perturbations [9, 10]. Identification methods [11, 12] are used to obtain approximate parameters of the mathematical model of an object with multiplicative uncertainty. The synthesized H_2 -regulator differs from the classical one in that additional input and output matrix transfer functions are used [13–15]. The latter are formed on the basis of a compromise between the quality of the system in nominal mode, the energy saving of the system and the robustness to internal changes in the object. The introduction of matrix weight transfer functions led to an increase in the order of the synthesized regulator, therefore a number of methods for reducing the order of the regulator were subsequently used [16–20].

Based on the results of mathematical modeling of systems with robust and local regulators [21, 22], the main characteristics of quality and stability were calculated and the response graphs of the systems were obtained for various types of perturbations.

Results and discussion

Analysis of the object of control, a mathematical model of an object

Modern dairy plants throughout the country are mostly equipped with lamellar pasteurization-cooling units of various types and constructions. A lamellar pasteurization-cooling unit is intended for continuous heating and pasteurizing of milk, cream and other liquid food products without losing the main properties such as protein, sugar and molecules of fat. The concept of their performance lies in the series flow from one tank into another, gradually mixing with the already heated milk, and then the milk is heated and maintained during an appropriate period of time at the temperature of pasteurization. After heating, the product is cooled and forwarded to other stages of processing or packaging.

Figure 1 shows a simplified scheme of production flows of a typical lamellar pasteurization-cooling unit. Here t_{1r} is the temperature of incoming raw milk, t_{1p} is the temperature of pasteurized milk, t_{1w} is the temperature of the heated milk, t_{1rec} is the temperature of recuperated milk, t_{10} is the temperature of cooled pasteurized milk, t_{2h} is the temperature of hot water, t_{2c} is the temperature of cooled water, m_1 is the consumption of milk, m_2 is the consumption of hot water, m_3 is the consumption of iced water, m_4 is the consumption of steam.

Automatic temperature regime control of a lamellar pasteurization-cooling unit is reduced to two local loops of temperature control for pasteurized and cooled milk (PID or PI) with a stabilized input flow. In terms of automation, the control object is multiply-connected, transient; the coordinates of the state are divided by spatial value, also, the object operates under permanent intensive external disturbances which are characterized by both deterministic and random components, the latter having a pigmented spectrum. In addition to the external perturbations which are shown in Figure 1, the quality of the output product is influenced by the acidity of the input product and the ambient temperature, which are not included into the control loop. Consequently, the use of the local regulators leads to quality degradation of the output product, and in some cases leads to re-pasteurization of the processed milk.

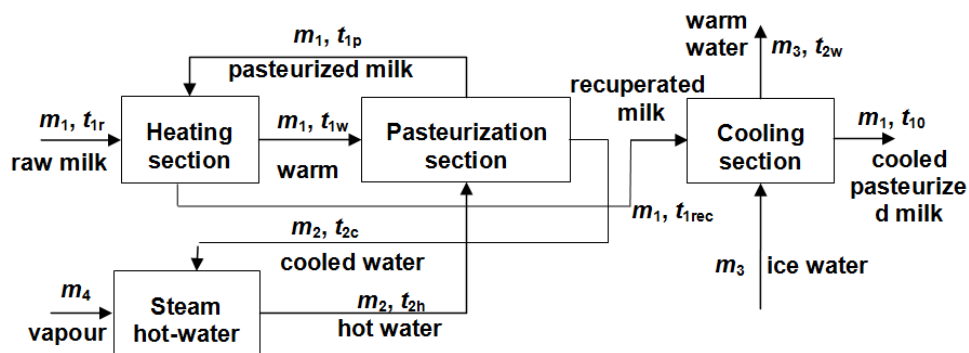


Figure 1. Scheme of the production flows in a lamellar pasteurization-cooling unit

The problem of developing a mathematical model of a production process control object is still being controversial. For the synthesis of an effective control system, a mathematical model is to describe the object as best as possible, which leads to large orders of systems of differential equations, a complex description of parameters and traceability of a large number of external and internal variables in a production object, and consequently, to the complex and lengthy control algorithm, whereas simplifying the mathematical model reduces the quality of control [22]. Therefore, an alternative in developing the mathematical model of a production control object is using different types of uncertainties, which, on the one hand, simplifies the nominal model of an object, while taking into consideration the allowance in such description and changes in the object itself, on the other hand.

A lamellar pasteurization-cooling unit can be simply described by a system of differential equations of the 7th-order with a multiplicative type of uncertainty, including both parametric changes in an object and unmodulated dynamics, which appeared as a result of reducing the order of differential equations. Let's convert the model of a lamellar pasteurization-cooling unit to the space of state variables, taking into consideration the task signals in addition to the perturbations:

$$\begin{cases} \dot{\mathbf{x}}(t) = \mathbf{A}\mathbf{x}(t) + \mathbf{B}_1 \begin{bmatrix} [\mathbf{w}(t) \ \mathbf{v}(t)]^T \\ \mathbf{r}(t) \end{bmatrix} + \mathbf{B}_2 \mathbf{u}(t), \\ \begin{bmatrix} \boldsymbol{\varepsilon}(t) \\ \mathbf{u}(t) \end{bmatrix} = \mathbf{C}_1 \mathbf{x}(t) + \mathbf{D}_{11} \begin{bmatrix} [\mathbf{w}(t) \ \mathbf{v}(t)]^T \\ \mathbf{r}(t) \end{bmatrix} + \mathbf{D}_{12} \mathbf{u}(t), \\ \boldsymbol{\varepsilon}(t) = \mathbf{C}_2 \mathbf{x}(t) + \mathbf{D}_{21} \begin{bmatrix} [\mathbf{w}(t) \ \mathbf{v}(t)]^T \\ \mathbf{r}(t) \end{bmatrix} + \mathbf{D}_{22} \mathbf{u}(t), \end{cases} \quad (1)$$

where $\mathbf{x}(t) = [\Delta t_{rec}, \Delta t_{1w}, \Delta t_{1p}, \Delta t_{2c}, \Delta t_{10}, \Delta t_{2w}, \Delta t_{2h}]^T$ is a state coordinate vector; $\mathbf{u}(t) = [\Delta m_3, \Delta m_4]^T$ is a vector of control, $\mathbf{w}(t) = [m_1, m_2, \Delta t_{1r}]$ is a vector of external perturbations; $\mathbf{v}(t) = [v_1(t), v_2(t)]$ is a vector of perturbations along the measuring circuit; $\mathbf{r}(t) = [\Delta r_1(t), \Delta r_2(t)]^T$ is a vector of the specified signals; $\mathbf{z}(t) = [\boldsymbol{\varepsilon}(t), \mathbf{u}(t)]^T$ is a vector of stabilized outputs; $\boldsymbol{\varepsilon}(t) = \mathbf{r}(t) - \mathbf{y}(t)$ is a vector of deviations from the specified signals; $\mathbf{y}(t) = [x_3(t), x_5(t)]^T$ is a vector of measurements.

All the matrix coefficients from (1) are determined on the basis of the aprior information about an object and as a result of identification [7-12]. The identification can be carried out by supplying pseudobinary signals to each input of the object and recording the output signals through the SCADA (Supervisory Control And Data Acquisition) program. The latter, through the PLC (Programmable Logic Controller) chain, is a field technology implemented by analog data transmission and industrial networks, receives information about the control object and executes a control signal. It is advisable to import the data into the Matlab software environment, where further processing will be carried out. Thus, for the A1-OXJI10 (OHL10) type lamellar pasteurization-cooling unit it is possible to determine and construct the basic matrix coefficients (1):

$$\mathbf{A} = 10^{-2} \cdot \begin{bmatrix} -23.31 & 0 & 20.75 & 0 & 0 & 0 & 0 \\ 0 & -23.31 & 2.56 & 0 & 0 & 0 & 0 \\ 0 & -2.25 & -22.47 & 0 & 0 & 0 & 24.72 \\ 0 & 24.31 & 0 & -69.44 & 0 & 0 & 45.14 \\ 3.07 & 0 & 0 & 0 & -10.57 & -54.02 & 0 \\ 7.32 & 0 & 0 & 0 & 20.05 & -27.10 & 0 \\ 0 & 0 & 0 & 19.16 & 0 & 0 & -19.16 \end{bmatrix},$$

$$\mathbf{B}_1 = [\mathbf{W}_w \mathbf{B}_1^w \quad \mathbf{B}_1^v \quad \mathbf{B}_1^r], \quad \mathbf{B}_1^v = [\mathbf{0}_{7 \times 2}], \quad \mathbf{B}_1^r = [\mathbf{0}_{7 \times 2}],$$

$$\mathbf{B}_2 = \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ -4.078 & 0 \\ 0 & 13.662 \end{bmatrix}, \quad \mathbf{B}_2 = \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ -4.078 & 0 \\ 0 & 13.662 \end{bmatrix}, \quad (2)$$

$$\mathbf{C}_1 = \begin{bmatrix} -\mathbf{C}_1^1 \\ \mathbf{0}_{2 \times 7} \end{bmatrix}, \quad \mathbf{C}_1^1 = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}, \quad \mathbf{C}_2 = -\mathbf{C}_1^1,$$

$$\mathbf{D}_{11} = \begin{bmatrix} \mathbf{0}_{2 \times 3} & \mathbf{W}_v \mathbf{I}_{2 \times 2} & \mathbf{I}_{2 \times 2} \\ \mathbf{0}_{2 \times 7} & & \end{bmatrix}; \quad \mathbf{D}_{12} = \begin{bmatrix} \mathbf{0}_{2 \times 2} \\ \mathbf{I}_{3 \times 3} \end{bmatrix}; \quad \mathbf{D}_{21} = [\mathbf{0}_{2 \times 3} \quad \mathbf{W}_v \mathbf{I}_{2 \times 2} \quad \mathbf{I}_{2 \times 2}]; \quad \mathbf{D}_{22} = [\mathbf{0}_{2 \times 2}].$$

Here $\mathbf{0}_{i \times j}$, $\mathbf{I}_{i \times j}$ are zero and unity dimension matrices $i \times j$ respectively; \mathbf{W}_w , \mathbf{W}_v are standardized weighting matrices of the intensity of external perturbations and noise measurements respectively. We might note that a control vector $\mathbf{u}(t)$ is additionally embedded into an output vector $\mathbf{z}(t)$ to restrict the signal of the former.

Synthesis of a robust optimal regulator

The functional chart of the control system is shown in Figure 2, where $\mathbf{G}(s)$, $\mathbf{G}_0(s)$ are transfer functions of the uncertainty object and the nominal object accordingly, obtained from (1), and $\mathbf{K}(s)$ is a transferable function of the regulator, $\Delta_{\mathbf{w}_0}(s)$ is a structural weighting uncertainty; s is a complex variable. Here, the mathematical model of the control object will be written as follows:

$$\mathbf{G}(s) = \mathbf{G}_0(s)(\mathbf{I} + \Delta_{\mathbf{w}_0}(s)), \quad \|\Delta_{\mathbf{w}_0}(s)\|_{\infty} < \gamma, \quad (3)$$

where γ is the uncertainty range.

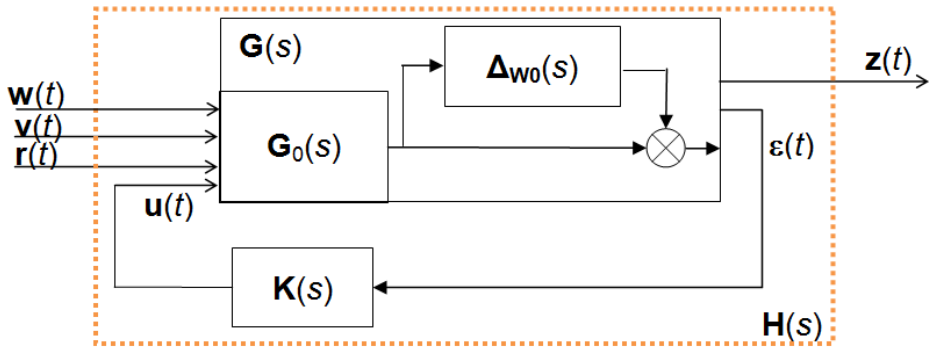


Figure 2. The functional chart of the control system

With regard to the above said, we can formulate the statement of the problem for the robust optimal control of a lamellar pasteurization-cooling unit: for a production object the mathematical model of which in the nominal mode is given by the system (1) with matrices (2), in the category of linear stabilizing controls

$$\mathbf{u} = \mathbf{K}(s)\boldsymbol{\varepsilon} \quad (4)$$

to find the optimal control which minimizes the specified quality criterion:

$$J = \min_{\mathbf{K}(s) \in \Omega} \|\mathbf{W}_L(s)\mathbf{H}(s)\mathbf{W}_R(s)\|_2, \quad (5)$$

where $\mathbf{H}(s)$ is the transfer function of the closed system, Ω is the area of stabilizable controls; $\mathbf{W}_L(s)$, $\mathbf{W}_R(s)$ are weighting matrices according to the outputs and inputs of the system. It is necessary to note that the weighting matrix $\mathbf{W}_L(s)$, specifies the quality of the system in the frequency range, and the matrix $\mathbf{W}_R(s)$ is a type of an input signal, in particular, one can specify a filter for an inhomogeneous signal spectrum. Thus, using criterion (5), the system minimizes the overall response pulse energy for the deterministic inputs, as well as the square root of the output dispersion for the specified dispersion of the input stochastic signal.

This problem has been solved in the state space for the standard H_2 problem [13-15], based on the 2-Riccati approach, with the following weighting matrices:

$$\mathbf{W}_L = \text{diag}\left(\frac{0.1}{50s+1}, \frac{0.1}{125s+1}, \frac{s}{500s+1}, \frac{s}{1000s+1}, 1, 1\right) \quad (6)$$

$$\mathbf{W}_R = \text{diag}\left(\frac{2.5}{2500s+1}, \frac{1.5}{2000s+1}, \frac{1}{200s+1}, \frac{s}{s+0.1}, \frac{s}{s+0.1}, 1, 1\right), \quad (7)$$

where $\text{diag}(\)$ marks the diagonal matrix, while the linear regulator happens to be of the 11th order. Analyzing the singular values of the transfer matrix of the regulator, it has been concluded that the regulator order can be reduced to the 6th [16–20]. The final regulator has

been chosen and its order has been reduced by the method of balanced reduction according to the criterion:

$$\|\mathbf{K} - \mathbf{K}_{red}\|_{\infty} \leq 2 \sum_{k=1}^n \sigma_k, \quad (8)$$

Where $\mathbf{K}(s)$, $\mathbf{K}_{red}(s)$ are the transfer functions of the output and the reduced regulator respectively, with a marginal error of 0.0335.

The regulator has been implemented in the range of state variables with the following matrices:

$$\mathbf{A}^{K_{red}} = 10^{-2} \cdot \begin{bmatrix} -0.88 & 0.52 & 0.33 & 0.59 & -5.65 & 0.67 \\ -3.51 & -388.41 & -265.61 & -35.26 & -8.09 & -18.69 \\ 0.47 & 266.78 & -3.49 & 3.46 & 10.08 & -1.81 \\ 0.25 & 52.73 & -6.25 & -1.14 & 28.34 & -2.42 \\ -5.42 & 13.64 & 1.05 & -11.09 & -184.56 & 130.86 \\ -0.39 & 30.69 & -1.60 & -0.24 & -125.39 & -3.48 \end{bmatrix},$$

$$\mathbf{B}^{K_{red}} = 10^{-2} \cdot \begin{bmatrix} 4.79 & 17.40 \\ 149.45 & -4.68 \\ -12.23 & -2.08 \\ -6.10 & -1.54 \\ -0.17 & 60.97 \\ -4.84 & 5.18 \end{bmatrix}, \quad (9)$$

$$\mathbf{C}^{K_{red}} = 10^{-2} \cdot \begin{bmatrix} 18.04 & -2.10 & -4.11 & -6.27 & 60.96 & -6.80 \\ 0.29 & 149.50 & 11.70 & 0.57 & 1.50 & 2.02 \end{bmatrix}, \quad \mathbf{D}^{K_{red}} = [\mathbf{0}_{2 \times 2}].$$

Results of the simulation

The simulation of a system with a synthesized robust optimal regulator and local PID and PI regulators for a nominal model and a model with maximum multiplicative uncertainty has been conducted. The parameters of local regulators have been synthesized according to the criterion of maximum perturbation filtering. Signals of disturbances have been applied to the system input throughout the time frame, with external disturbances simulated by a stochastic and deterministic component, and at the time of 75 sec the tasks from zero to 2 °C and 1 °C have changed respectively. The simulation results are shown in Fig. 3-5 and comparative characteristics are summarized in Table 1.

Table 1

Comparative characteristics of systems with H_2 - and PID-PI regulators

Characteristics	Type of regulator	
	H_2 -regulator	PID-PI regulators
Maximum deviation	$\varepsilon_1 = 2.1$ °C $\varepsilon_2 = 1.0$ °C $u_1 = 0.2$ kg/sec $u_2 = 0.9$ kg/sec	$\varepsilon_1 = 2.0$ °C $\varepsilon_2 = 1.0$ °C $u_1 = 1.0$ kg/sec $u_2 = 1.9$ kg/sec
Medium-quadratic deviation	$D\varepsilon_1 = 0.2$ °C $D\varepsilon_2 = 0.1$ °C $Du_1 = 0.04$ kg/sec $Du_2 = 0.1$ kg/sec	$D\varepsilon_1 = 0.4$ °C $D\varepsilon_2 = 0.1$ °C $Du_1 = 0.2$ kg/sec $Du_2 = 0.4$ kg/sec
Stability margin	0.08	0.12
$\ H_{w\varepsilon}(s)\ _2$	0.25	0.34
$\ H_{v\varepsilon}(s)\ _2$	1.02	2.25
$\ H_{[w v]k}(s)\ _\infty$	1.13	5.27
γ	0.56	0.13
$\ S(s)\ _\infty$	1.63	5.29

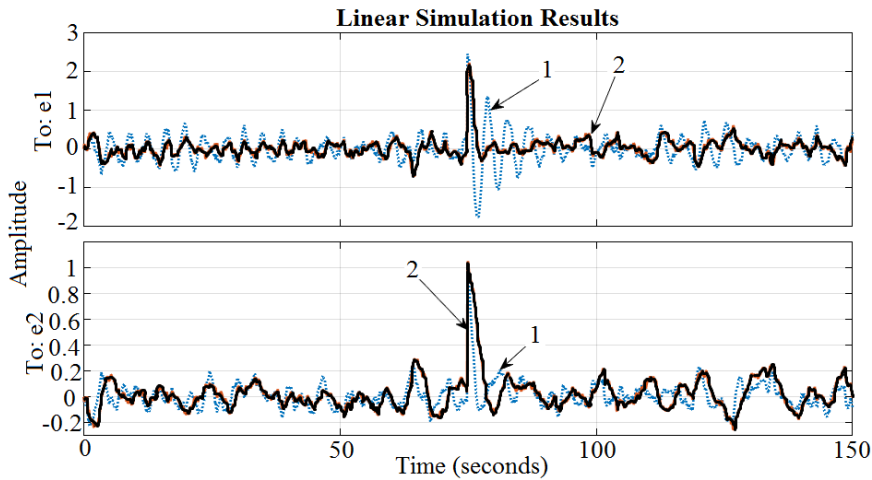


Figure 3. Deviation of pasteurization and cooling temperatures:
1 – System with PID-PI regulators; 2 – System with H_2 -regulators

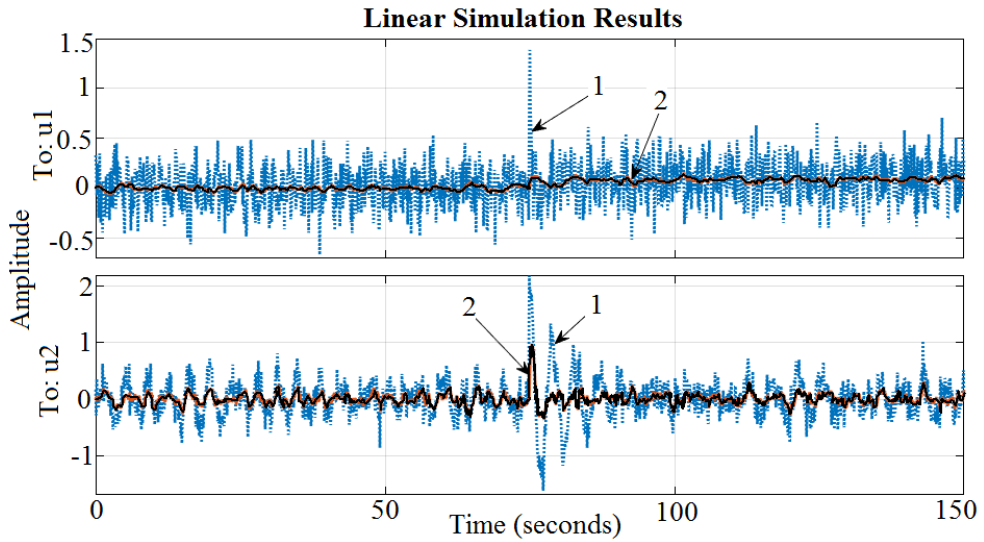


Figure 4. Deviation of control signals:
1 – System with PID-PI regulators; 2 – System with H_2 -regulators

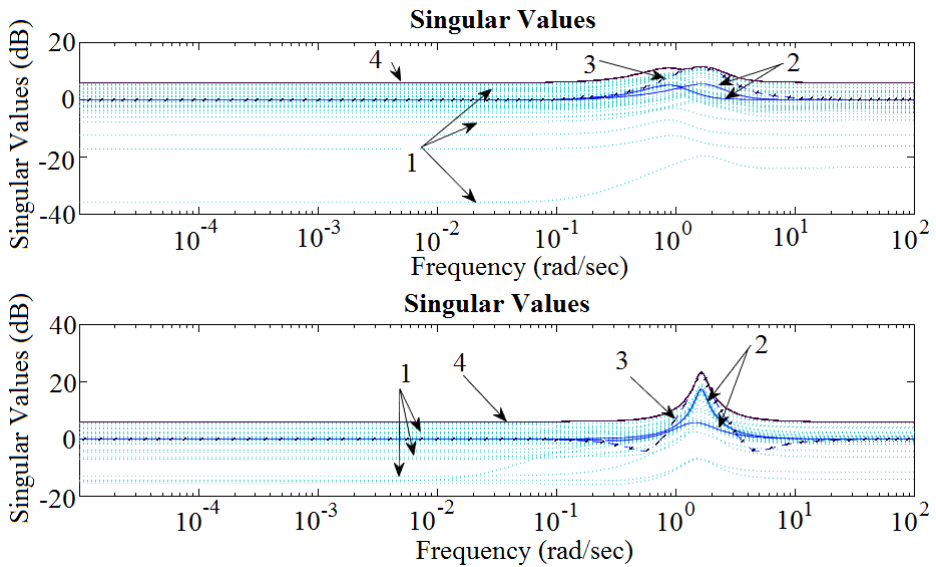


Figure 5. Singular values plot of dynamic system with uncertainty:
1 – System with sampled uncertainty; 2 – Nominal system; 3 – System with worst uncertainty;
4 – Worst-case gain (upper bound)

The H_2 -regulator system shows better quality and energy-efficient performance, since the norms characterizing the quality of the system have decreased almost twice, and the scope of uncertainty has increased fourfold. In addition, the H_∞ -norms of the sensitivity transfer functions $S(s)$ for such a system are lower has tripled, which confirms the robust properties of the system. Also, the dispersion of the first regulated quantity was reduced twice, and the dispersion of control signals decreased respectively five and four times. In Fig. 5 is shown graphical worst-case gain analysis [21, 22] synthesized system, in particular the curve of upper bound is the envelope produced by finding the highest gain within the uncertainty at each frequency. So, the time and frequency analysis of the system proved the effectiveness of the synthesized control system.

Conclusion

A lamellar pasteurization-cooling unit performs under the conditions of uncertainty of both the structure and parameters of the object, and intense external perturbations. Advance in efficiency of the control system of lamellar pasteurization-cooling units is possible by constructing a multidimensional optimal regulator in accordance with the H_2 -norm criterion. The mathematical model of the control object has been presented and reduced to the standard setting of the H_2 -optimization with the input and output weighting matrices while the synthesized regulator in the space of the state variables has been reduced to the 6th order. The simulation of the system conducted by the H_2 -regulator has shown its effectiveness compared to the local PID-PI regulators.

Further research is aimed at automatically revealing the conditions for the applicability of robust-optimal regulators for building an information system to support management decisions.

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Representation of agricultural producers' interests: substantiation of the research construct

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Abstract

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Introduction. The research aims to substantiate a construct of the scientific research which enables assess the associated agricultural producers' involvement in agricultural policy-making processes.

Materials and methods. Methods of scientific discourse analysis, survey of agricultural producers, statistical data analysis, systematization and synthesis of scientific insights were used. The theoretical background is based on analysis of management theories explaining a nature of inter-organizational interaction.

Results and discussion. Representation of agricultural producers' interests in policy making processes is inappropriate. We chose Lithuania as example and found that even 85.6 percent of farmers are completely not members of any association or union and only about 10 percent of them participate in activities of organizations of agricultural area. The research results show that in the context of EU financial support for agriculture the problem of stakeholder participation in policy making processes deforms the opportunities of big and small farmers to defend their interests. Participative and Collaborative Governance and concept of partnership and inter-organizational collaboration were achieved i) by distinguishing characteristic groups of associated agricultural producer organizations' participation in agricultural policy making processes, ii) by compiling a scheme of research on the balance of need satisfaction and interest expression of associated agricultural producers, and iii) by forming theory-based battery of interview questions for further qualitative survey was. During analyzing results of research it was found that the implementation of interests based on needs should become a core task for policy makers. In order to do so, it must be ensured that stakeholders' influential power is balanced, and the needs of all interest groups are appropriately evaluated. The research results show that the assumptions for better opportunities to take agricultural stakeholder needs into consideration when forming and implementing agricultural policy could be strengthened.

Conclusions. Research allows systematically gather qualitative data and better substantiates recommendations to politicians and representatives of agricultural producer associations.

Introduction

A competitive advantage of organization mostly is influenced by management decisions whereas in agricultural sector the competitiveness is distorted due to the EU support opportunities which essentially are only distributed taking the size of a given farm into consideration [7; 40; 41; 37]. Due to this reason, the business and operating conditions of larger-scale farmers are improved quicker than those of smaller ones. Financial support for larger-scale farms allows them to expand, purchase more or more advanced agricultural machinery, implement technological innovations etc. [25; 22; 19].

Furthermore, the differences in farming conditions are influenced by insufficiently justified agricultural policy priorities on a national level in most of post-Soviet countries, and Baltic countries are among them [6; 25; 37]. The support system in agriculture is formed to support farmers using the same principle without considering their needs, activity opportunities and objective constraints. On the other hand, even though farmers unite into associations and other organized entities, the interests of some of them in the context of agricultural policy are not being protected sufficiently [26].

With the start of a new EU financial period coming near in 2020, the abovementioned issues become especially significant. In addition to that, scientific research on administration effectiveness, business competitiveness and balanced representation of stakeholder interests in making decisions remain important as well [29; 22; 7]. Considering relevance, the aim of the article was defined: on the bases of scientific literature and results of the survey to substantiate a research construct which would enable to assess the associated agricultural producers' involvement in agricultural policy-making processes.

The research developed in later stages would allow the agricultural producers to better protect their interests in pursuing competitiveness in agricultural business and farming. It would also enable the political decision-makers to better understand the nature of stakeholders' needs and differences between them.

Materials and methods

With the aim to substantiate a research construct which would enable to assess the associated agricultural producers' involvement in agricultural policy-making processes, methods of i) scientific discourse analysis, ii) survey of farmers, iii) statistical analysis of primary data, iv) statistical analysis of secondary data, and v) systematization and synthesis of insights were used. The theoretical background of the article is based on management theories explaining a nature of inter-organizational interaction, and that are: Transaction Costs Economics theory [18; 27; 39], Stakeholders theory [11; 21; 28] and Network theory [2; 3; 23; 32], whereas principles of interest representation and stakeholders' participation in policy making and implementation processes are explained by the concepts of participatory and collaborative governance [9; 20; 29], also social partnership and inter-organizational collaboration ideas [31; 34; 17] were taken into consideration. Common agricultural policy (CAP) effect on farm development was based on statistical data of Eurostat, and survey of agricultural producers in Lithuania as one of exemplar was completed with the aim to reveal context and relevance of the research construct.

Results and discussion

Research context: Common agricultural policy effect on farm development in Lithuanian

The peculiarities of agriculture in Lithuania reduce the agricultural sector's resistance to negative factors both inside and outside the country and sector. These peculiarities were influenced by various conditions, the most significant of which are the implementation of Common Agricultural Policy (CAP) based on the EU support, specifics of national priorities in agriculture and lack of unity between agricultural producers in defending their essential interests.

The criticism on common agricultural policy, especially the imperfectness of direct payment system and its inability to implement the set goals is sore for over a decade [14; 5;40; 41; 35]. On one hand, the direct payment system is criticized by the society for spending public funds and constantly facing environmental and animal well-being problems. On the other hand, farmers are dissatisfied with the increasing inequality of income and, in their opinion, unjust distribution of direct payment system elements [22].

Back in 2005-2010, Lithuania was already one of the few EU countries with dominant effect of farm structure polarization, where the number of big farms (over 100 ha) doubled, the number of small farms (under 5 ha) increased slightly while the number of average farms decreased [25]. This phenomenon indicated an instable agricultural structure, the foundation of which (the average farms) was vulnerable and of low viability.

In 2016, compared to 2005, the number of farms over 100 ha and more in size increased by 114 percent in Lithuania, while in the EU-28 this number was only 11 percent on average (Figure 1). The number of farms of 10 to 100 ha decreased by 32.2 percent in this period while the number increased by 13 percent in the EU. Lastly, the number of farms under 10 ha decreased both in the EU and Lithuania – 33.2 and 44.9 percent decrease respectively. It should be noted that in Lithuania, the number of farms under 10 ha and farms between 10 and 100 ha decreased twice as quickly as in rest of the EU.

According to Lithuanian agricultural structure, in 2016 there were 107.8 thousand farms under 10ha. The number of farms over 100 ha was only 5.3 thousand, however, their owners owned almost 3.5 times more area by hectares. In other words, currently in Lithuania, 3.5 percent of landowners control more than 50 percent of all agricultural land utilities.

The changes in Lithuanian agricultural structure became clear after implementing the direct payment system and applying a one-time payment-for-area scheme [25]. A support system based on payments for owned agricultural land utility area in hectares had a strong influence on the changes in types of production generated in farms. Farmers significantly increased investment into grain growing as an activity that requires big areas of land. This allowed to ensure direct financial returns through direct payments with relatively low work and capital input requirements per 1 ha of land [37]. The consequences of decision to grow more grain are especially visible comparing years 2005 and 2016. In 2016, Lithuania became a leader in the change of grain growing farms amongst all EU member countries. In this time period, the number of grain growing farms in Lithuania increased by 346 percent while the growth in the EU was only 7 percent on average. It should be emphasized that the area of arable land used in farms increased as well – an increase of 186 percent is observed.

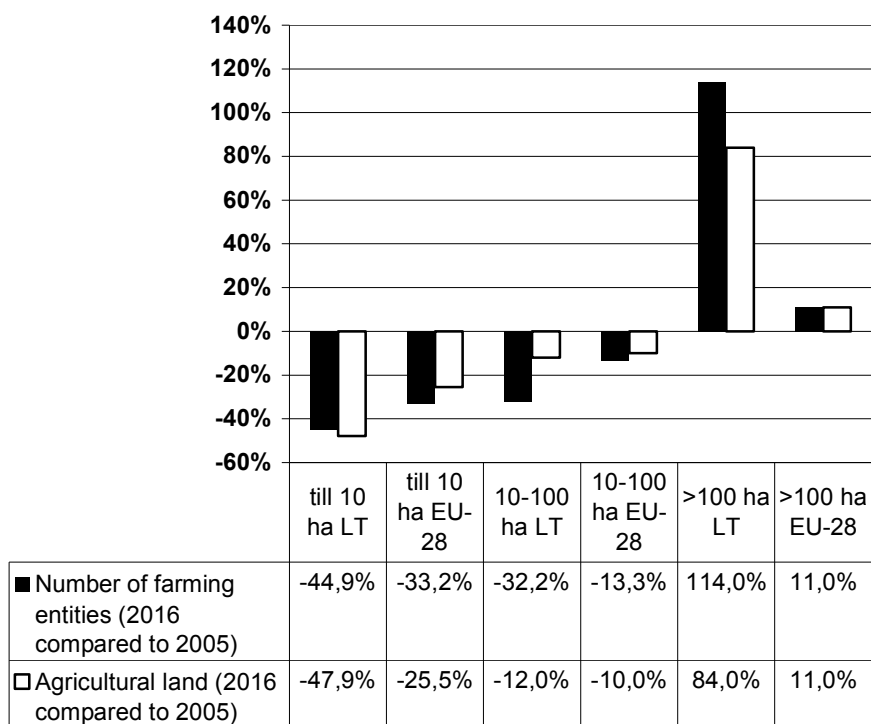


Figure 1. The change in the number of farms and farmland in different groups by size in Lithuania and on average in EU-28, 2016 compared to 2005.

Source: authors compilation based on EUROSTAT.

The support measures of common agricultural policy had an influence on Lithuanian agricultural structure changes too. Some national level rules of financial support for agriculture made it easier for larger-scale farms, especially those over 100 ha to receive bigger support. Due to production potential being directly proportional to farm size, big farmers became more attractive to financial credit companies while the owners of small farms were assigned a higher risk group and lost a part of opportunities to acquire or develop their competitive advantage by investing into new activities or development.

Summing it up, the abovementioned reasons and conditions in Lithuania caused: i) agricultural structure changes and decrease in farm numbers; ii) vulnerability of farms growing other production than grain; iii) competitive imbalance between farms considering both size and production type; iv) contraposition of small and big farmers; v) more evident display of social inequality; vi) imbalance of agricultural producers' interest representation in agricultural policy making observed through political decisions that insufficiently satisfy the needs and interests of small farmers. However, in order to objectively evaluate if and how the size of the farm is related to the representation of interests of its owner in agricultural policy making and to provide recommendations which would allow to ensure adequate satisfaction of agricultural producers' needs, a definition of small, average and big farms has to be formed.

The area of the farm is one of the most commonly used criteria in statistical, economic and political analyses which determine the boundaries between small and other farms. Small farms are defined differently in different countries: fewer than 2 ha, under 5 ha, under 10 ha of land utilities or 10 percent of smallest farms that declare land utilities [6; 19; 10]. Thus, if an agreement was made in Lithuania on what criteria would allow to unambiguously classify farms by their size, it would be possible to more clearly evaluate the potency of farmer group interest representation and to pursue a common societal well-being by executing a more effective and favorable agricultural policy.

Relevance of agricultural producers' interests representation research

A survey of agricultural producers was carried out to determine the relevance of scientific research problem. An original representative empirical data were collected by experienced research subcontractor. Population of Lithuanian farmers equals to N=138.9 thousand. Calculated representative population under statistical conditions of 3 percent error ($\epsilon=0.05$) and 95 percent ($p=0.5$) confidence level is $n=1059$. Respondents were selected using systemic sampling of research subcontractors' database. Data were collected using telephone interviews of Lithuanian farmers in January-February 2017. Potential respondents had been telephoned 3211 times, 1491 times without response, 612 farmers rejected the suggestion to take part in the interview. Finally, 1108 interviews were found suitable for further investigations which satisfy defined statistical conditions.

The obtained data was processed with descriptive statistical analysis. The percentage distribution of respondents' answers was calculated, comparing data between the groups by using χ^2 test (significance level $p < 0.05$). The sample size of the study allows ensuring that the statistical error of the results does not exceed 3.1 percent. Statistical analysis of data was performed using the SPSS 20.0 program. A two-stage variable χ^2 independence test was performed to determine whether the respondent's characteristics (sex, age, etc.) affect the distribution of answers to questions. Only those answers are used as evidence, in which the test showed that the distribution of answers depends on the respondents' characteristics.

The study involved 57.7 percent men and 42.3 percent women. The majority of surveyed farmers (38.3 percent) were respondents aged from 55 to 64; the second age group (27.6 percent) was farmers aged between 45 and 54, respondents of 65 years and older composed 23.9 percent. The smallest group of respondents is represented by youngest farmers: 1.1 percent is up to 35 years and 9.1 percent aged between 35 and 44. The majority of respondents (34.5 percent) had acquired professional education; farmers with acquired upper and secondary education composed respectively 23.7 percent and 21.4 percent. The smallest group of respondents according to their education consists of respondents with lower secondary (4.6 percent) and primary education (1.6 percent). The majority (88.4 percent) of the surveyed farmers acquired education before 1990 (or in the Soviet period), 10 percent – before the Lithuania's accession to the EU (i.e. in the period of 1990–2004) and 1.6 percent in 2005 or later, i.e. after Lithuania's accession to the EU.

The majority of respondents (44.8 percent) are farmers whose farm size is up to 20 hectares (ha); 32.1 percent – from 20.1 to 50 ha; 13.7 percent – from 50.1 to 100 ha. The smallest part of the respondents are farmers with farms of 100.1 to 500 ha (9.2 percent) and more than 500.1 ha (0.2 percent).

According to the criterion of the duration of the activity, almost half of the surveyed farmers (46.6 percent) started their farming activities 21 year ago or even earlier, a similar proportion of respondents (43.1 percent) – from 11 to 20 years ago, and the youngest farms with experience 10 and less years of farming composed 10.3 percent. More than half of the

respondents (54.1 percent) have mixed (both crop and livestock) farms, 21.5 percent are crop farmers, and livestock farmers compose 13.3 percent.

By summarizing the general statistical characteristics of the survey, it can be stated that given data is representative.

Talking about research insights, it should be emphasized that representation of agricultural producers' interests in is inappropriate. Even 85.6 percent of farmers are not members of any organization (e.g. association, union, confederation, etc.) and only about 10 percent of farmers participate in activities of organizations of their professional area (Figure 2).

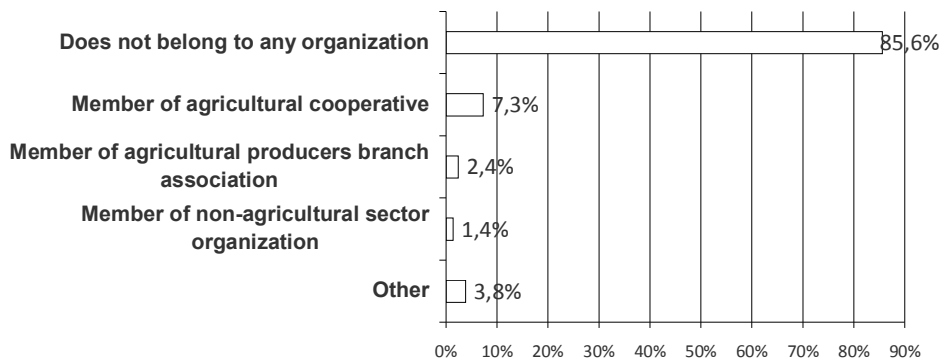


Figure 2. Agricultural producers' participation in organized activities.

Source: authors.

A similar portion of farmers shows personal initiative to cooperate having an aim to protect common interests (Table 1).

On the other hand, 53.8 percent of respondents are ready to contribute in case of joint activity were organized in their community or rural area, or area of their professional expertise (Figure 3).

Table 1
Distribution of answers to the question "Have you ever asked other farmers to cooperate with the aim to protect common interests?"

	Frequency	Percent
Yes	147	13,3
No	958	86,4
Other	3	0,3
Total	1108	100

Source: authors.

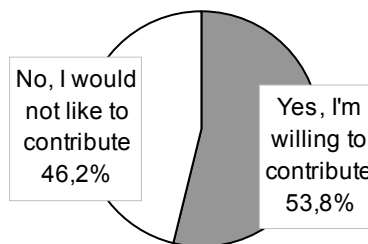


Figure 3. Farmers' willingness to contribute in joint activity.

Source: authors.

The contradiction between attitudes and behavior of farmers can lead to a question of what determines the situation that farmers do not enter organizations for joint activities although they have willingness for this. In order to answer this question, qualitative research construct is modeled and presented further.

Construct of research on representation of associated agricultural producers' interests: theoretical background

The plan of the research on associated agricultural producers' opportunities to satisfy the needs of represented farmers was based on a theoretical basis which would allow to explain the relationship between the society, country and business and would allow to understand what principles and assumptions should be followed to coordinate the goals of all sides.

Management theory analysis has allowed to distinguish three theories complying with this goal: Transaction Costs Economics theory, Stakeholders theory and Network theory, whereas principles of interest representation and stakeholders' participation in policy making and implementation processes are explained by the concepts of participatory and collaborative governance.

In this context, social partnership and interorganizational collaboration ideas were taken into consideration. They allowed to emphasize the essential goal and principle assumptions of joint actions of all stakeholders.

Transaction Costs Economics theory. Transactions costs economics theory (TCE) is based on specific assumptions. The first assumption states that an individual's behavior is opportunistic, and "self-interest is unconstrained by morality" [27]. The second assumption regards the requirement for success. Here, "efficiency" within predefined rules of the game is the criterion that determines the desirability of the outcome [39]. However, actors will not behave opportunistically by all means. The probability of opportunism occurring increases as asset specificity increases [18]. „Opportunism occurs when outcomes are highly uncertain, reputation is difficult to establish, and the payoff from opportunism in the present period outweighs the discounted present value of future cooperation“[18]. On the other hand, organizations have the ability to reduce opportunism through hierarchical control [15]. Thus, collaborative activities between the transaction parties are of major importance to the economic results the organization achieves. However, positive results are not always achieved. For example, when the number of interacting sides with influential power is low, competition occurs. It is especially relevant in the context of associated agricultural producer organizations and their influence on country-level decisions on agricultural sector. Ensuring that all stakeholders directly related to the decision are able to adequately participate in decision making processes becomes a crucial factor.

Stakeholder Theory. The Stakeholder Theory (SHT) connects the economic and social aspects of an organization and allows explaining the nature of relationships important to the existence of the organization [11]. According to SHT, the interests of all stakeholders are important, thus there should be no dominant interests [21]. An organization which takes into consideration the interests of all stakeholders sooner or later wins the competitive battle against an organization which only considers limited interests or bestows privilege on a particular interest group [8]. On an interorganizational level, SHT allows to solve the problem of organizational relations and interaction. The selection and inclusion of associated stakeholders should depend on the relevant issue and tasks being solved by the

organization in given circumstances. With this goal in mind, Mitchell et al. offer to determine to what extent the stakeholders are significant in the organization, evaluating three attributes of organizational relations: 1) power to influence the organization, 2) legitimacy of the relationship between organization and the stakeholder and 3) urgency of reacting to stakeholders' demands [28]. Stakeholders that correspond with only one attribute are called latent; those that correspond with two attributes are called expectant while those that correspond with all the attributes are called definitive stakeholders. It is also possible that a group or organization does not correspond with any of the attributes, in which case they are considered potential stakeholders. It should be noted that power, legitimacy and urgency can change depending on circumstances. Due to this reason, attributes may be gained or lost [28]. Thus, the significance of a stakeholder should be evaluated every time taking into consideration both changes and reality. Moreover, stakeholders can be external and internal, part of which can have overlapping interests. This way, different stakeholders may have different opportunities for creating mutual benefit in the stakeholder relationship [30].

Frooman refills SHT by claiming that stakeholders tend to influence organization management and decision making: "The appropriateness of a stakeholder's claim may not matter nearly as much as the ability of the stakeholder to affect the direction of the firm." [12, p. 193]. Therefore, such characteristics of interaction as participation basis and relationship structure should be taken into account for stakeholder analysis and mapping. A proper understanding of stakeholders' interests and power is crucial for efficiency of organization management.

The contribution of SHT should be exclusively mentioned when speaking about public sector organizations. In this case, the term "stakeholders" covers the whole society or especially large parts of it. Stakeholder engagement in solving issues of societal well-being can therefore manifest through direct participation in activities of non-governmental organizations, government bodies etc. (e. g. decision making) or indirect participation – incorporating significant actors into stakeholder networks.

Network theory. Representatives of political science and sociology employ the metaphor of network for explanation of political decision-making processes [32]. Network is a dynamic structure involving entities in different volumes and intensities. Networked organizations create a system of dependent variables without having a permanent organizational structure [2].

Concept of network theory was based by Kickert et al. [23], while Agranof and McGuire [3] processed the acquired empirical data and suggested a model of public network management. The network theory states that the performance of an organization is not based on hierarchical structures only, but on interaction between the components of the network. Therefore, network theory emphasizes the importance of facilitation, which is much more important in public sector. Facilitators must foster the members of the network, organize joint meetings and act as mediators in disputes; also, they must avoid supporting suggestions of particular interest groups and making one-man decisions [23]. The success of network structures is largely determined by the executives of organizations who should assume the function of a network conductor which is to create, manage and employ vertical as well as horizontal linkages among stakeholders [3].

The difference between Network theory and SHT and TCE is that it discusses subject relations, their directions and characteristics of the whole network rather than the interaction between actors and their influence on one another.

The principle assumptions of all three theories are widely reflected in participatory and collaborative governance concepts which are important to consider to reasonably examine the issue of stakeholder participation in policy making processes.

Concepts of participatory and collaborative governance. Collaborative governance is defined as a structure and process of public policy decision making that involves various stakeholders to carry out a public purpose. Meanwhile, participatory governance is considered as involvement of public, private profit and NGO actors who are not normally concerned with decision making [9; 29]. While participatory government is more focused on questions on government counseling with stakeholders, collaborative governance emphasizes the process of working together in particular. Both conceptions speak about participation and collaboration in making policy decisions and assessment of social impact. However, both of them have attributes characteristic only to one or another. According to Huxham, „collaboration carries ideological connotations associated with participation and empowerment. [...] Participation generally means engagement of stakeholders in the decision-making processes that affect them.“ [20, p. 340].

Concepts of collaborative and participatory governance deals with stakeholder inclusion into decision making processes as a way to increase the social and economic efficiency of the formed policy [4].

In order to implement collaborative governance conception in practice, it should be accepted that public interest and overcoming society's problems is of highest importance. In reality, it is complicated because interest groups compete with one another on a political level. It is hard for interest groups to give up on adversarialism and corporatism just like it is hard for the government to give up on managerialism [13].

Successful collaboration between stakeholders and the government depends on engagement of key stakeholders because weak engagement of stakeholders undermines the legitimacy of collaborative outcomes. Based on scientific research, authors state that exclusion of stakeholders can lead to situation where alternative forum will be formed [4]. Thus, it makes sense that the results of collaboration become distorted while the decisions that solve social and economic problems and due to which intersectoral collaboration takes place are usually inefficient.

Therefore, it is extremely important to find a way to ensure a balanced stakeholder participation in policy making in every case.

General provisions of inter-organizational interaction. The main value of partnership and inter-organizational collaboration is the effect of manifold synergy between actors, the goal they seek and processes they perform. Partnership is intended to implement social, economic and political programs and to solve problems common to stakeholders while collaboration is mainly characterized by the time given for joint work, especially to reach high level of trust and joint resources, from material to intellectual [31].

In social partnership, joint activity of organizations functioning in different sectors is of the highest value [34]; the competitive advantage is gained when neither partner can be changed or eliminated due to its unique position [33]. Partners that share common interests *and* joint goal rise to the next level of integration, the so called inter-organizational collaboration. As collaboration is a voluntary commitment in its nature, joint action requires stakeholders' commitment to behave on a non-competitive basis [17]. As a result, the live involvement of actors from organizations participating in joint activities, equal status in decision-making, efficiency of internal communication and continuous and

reciprocal informative relations with a target group are of highest importance in collaboration [38; 16].

The more intensively the organizations are involved into joint activities, the closer relations between them are formed and the higher joint results can be expected [36]. The process of implementation of partnerships and collaboration is full of difficulties. Many partnerships collapse due to bad understanding, incorrect allocation of costs and benefits, and distrust [1]. Thus, the principle assumptions of partnership and collaboration formed by scientists and verified by practitioners should be referred to by stakeholders with joint or overlapping goals.

Methodological substantiation of the research construct

The qualitative research methodological construct is based on analysis of beforementioned theories. It allows to identify the characteristics of associated agricultural producers' participation in agriculture policy making processes through economic benefit, engagement and commitment, influential power, nature of reciprocal relations and potential and constraints of collaboration (Figure 4.)

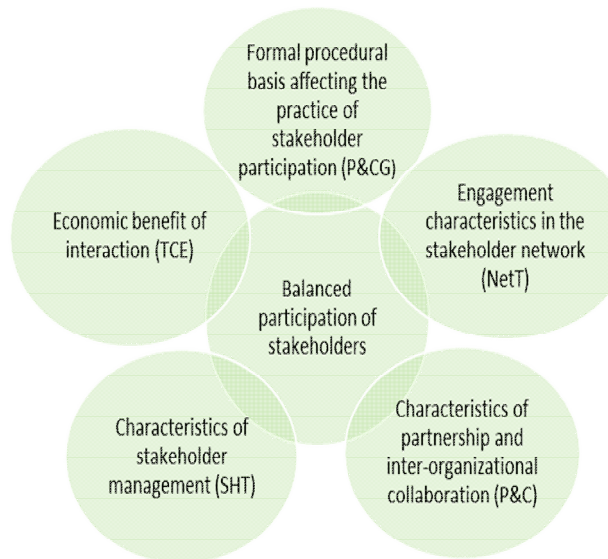


Figure 4. Groups of characteristics of associated agricultural producer organizations' participation in agricultural policy making processes.

Source: authors.

The distinguished characteristics of associated agricultural producer groups form a basis to study the specifics of such producers' participation in agricultural policy making and to prepare detailed instrumentation for research on the balance of the satisfaction of their needs and expression of interests. The instrumentation is schematically depicted in Figure 5.

The hypotheses of the research could be verified by a quantitative research. However, it is not the goal of this article and the instrumentation for quantitative research is not discussed further in the article.

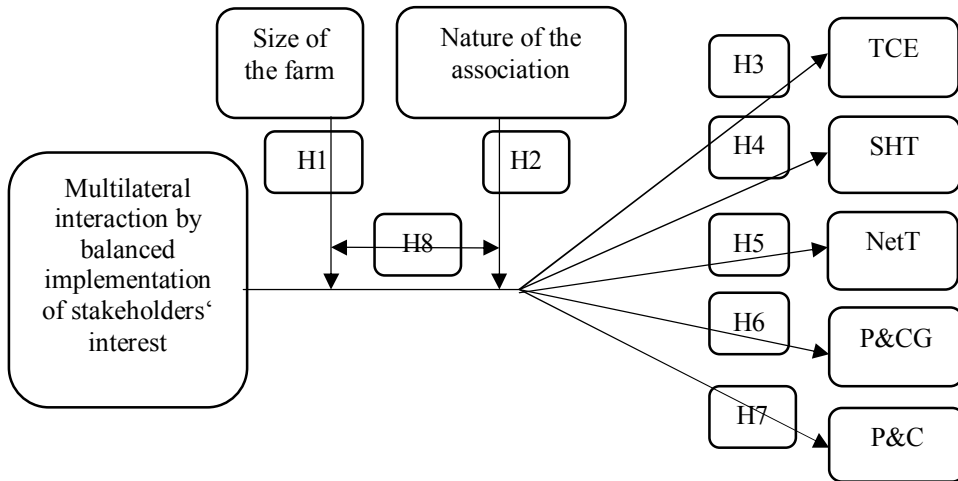


Figure 5. The scheme of research on the balance of associated agricultural producers' need satisfaction and interest expression.

Source: authors.

In order to determine what opportunities associated agricultural producer organizations have to express the needs and interests of their represented members, an expert, semi-structured interview of farmer association leaders would be valuable. The interview would be carried out in a homogenous sample because all agricultural producer organizations in Lithuania and the EU have equal legal opportunities to participate in the policy making and implementation processes while the leaders of associations can take on the initiative in intersectoral activities in order to better meet the farmers' needs.

The interview questions were shaped on theoretical approaches discussed in the section above. Theory-based battery of research questions are shown at a Table 2.

Table 2

A construct of an interview: theory-based battery of research questions

Q1 – <i>Transaction Costs Economics theory (TCE):</i>
What economic benefit the associations achieve both separately and together and what benefit could they expect from participating in policy making processes?
Q2 - <i>Stakeholder Theory (SHT):</i>
How are the farmers' needs and expectations, and association's interests taken into account when forming agricultural policy at the State level?
Q3 - <i>Network Theory:</i>
How organized and enabling is the structure of associated agricultural producer network?
Q4 - <i>Concepts of Participative and Collaborative Governance (P&CG):</i>
What structures and processes ensure the engagement of stakeholders of different sector, activity, volume and skills in the agricultural policy making processes?
Q5 - <i>Partnership and inter-organizational collaboration (P&C):</i>
How satisfied are the agricultural producers with their reciprocal partnership and interorganizational and interinstitutional collaboration results and process?

Source: authors.

The interview is designed to collect qualitative data required to better understand the problem context of agricultural producers' expression of interest.

The questions of Q1 group are meant to receive information about how the representatives of associated agricultural producers evaluate the opportunity to express the economic needs and interests of members they represent; if they have a possibility to initialize decisions based on needs and interests and propose decision corrections; if they collaborate with other associated agrarian organizations etc.

The questions of Q2 group help to find out if the needs expressed by agricultural producers and their associated organizations are held equally important in making agricultural policy decisions; how dominant interests are balanced out; how less active associated organizations of agricultural producers are included etc.

Q3 group's questions are meant to determine the existing relation structure by the power to influence agricultural policy decisions on a state level; how interorganizational and interinstitutional meetings between associated agricultural producer organizations are organized; what the essential characteristics of interorganizational relations in the agricultural producer representatives network are etc.

Q4 group's questions help to ascertain the principles of stakeholder engagement the governmental institutions follow and to determine if this procedure allows to ensure a balanced expression of interests as well as to find out what problems are solved by joint work between groups or institutions etc.

Questions of Q5 group are designed to receive information on the level of trust between agricultural producer organizations; what synergy stakeholder cooperation creates; what prevents joining intellectual, material and other resources to achieve both agricultural policy decisions that satisfy needs and interests and efficiency and effectiveness of activity etc.

Semi-structure interview provides the researcher with the opportunity to shift the conversation to relevant questions, ask additional questions or clarifications. Therefore, this interview should not be taken as an instruction but rather guidelines that facilitate the researchers' work and allow to maintain the theoretical methodological integrity of the research.

Conclusions

The analysis of scientific literature allows to state that a scientific and practical problem of stakeholder participation in policy making processes exists. In the context of the common agricultural policy of the EU and particularly in the context of EU financial support for agriculture, this problem is faced by a wide circle of stakeholders and becomes especially sore because it deforms the opportunities of big and small farmers to defend their interests.

In order to solve this problem, the article forms a theoretically and methodologically substantiated construct of associated agricultural stakeholder organizations' influential power and participation in agricultural policy making. Based on the Transaction Costs Economics theory, Stakeholder Theory, Network Theory as well as the concept of Participative and Collaborative Governance and concept of partnership and inter-organizational collaboration, the following were achieved:

- a. Characteristic groups of associated agricultural producer organizations' participation in agricultural policy making processes were distinguished;
- b. A scheme of research on the balance of need satisfaction and interest expression of associated agricultural producers was compiled;

- c. A theory-based battery of interview questions for further research of stakeholder in agriculture was formed.

Research proposed in the article could strengthen the assumptions for better opportunities to take agricultural stakeholder needs into consideration when forming and implementing agricultural policy. It should be emphasized that the implementation of interests based on needs, not wishes, principles or intent should become a core task for policy makers. In order to do so, it must be ensured that stakeholders' influential power is balanced, and the needs of all interest groups are appropriately evaluated.

Research on representation of agricultural producers' interests, conducted based on the theoretical and methodological construct of the research would allow to systematically gather qualitative data and better substantiate recommendations to politicians and representatives of agricultural producer associations who seek to more efficiently engage and participate in agricultural politics.

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Анотації

Харчові технології

Вплив метилжасмонату, саліцилової кислоти та аскорбінової кислоти на якісні показники полуничних плодів (*Fragaria x ananassa* Duch) під час холодного зберігання

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Вступ. Проведені дослідження з метою вивчення комбінованого ефекту розчину метилжасмонату, саліцилової кислоти та аскорбінової кислоти на зберігання полуничних плодів.

Матеріали та методи. Антоціани кількісно визначені рН-диференційованим методом. Загальні фенольні сполуки визначали за допомогою реагенту Фоліна-Цикальте. Аналіз FRAP (відновлення флюоресценції після фотознебарвлення) застосовували для визначення антиоксидантної активності. Визначення окремих антоціанів проводили за допомогою високоефективної рідинної хроматографії (HPLC) із використанням рідинного хроматографа марки Varian-Prostar-500. Аналіз текстури полуниці проводили з використанням аналізатора текстур.

Результати і обговорення. Досліджено вплив комбінованого розчину метилового жасмонату (MJ), саліцилової кислоти (SA) та аскорбінової кислоти (AA) на зберігання полуничних плодів (сортів Вікторії та Камарози). Оброблення за допомогою MJ, SA та AA позитивно вплинуло на рівень вмісту вітаміну С у плодах полуниці під час зберігання. Загальні антоціани в контрольних зразках сорту Вікторії поступово знижувались з $21,35 \pm 1,06$ до $13,35 \pm 0,66$ мг/100 г на 13-й день зберігання. Стосовно оброблених зразків, то вміст антоціанів зменшувався до $15,49 \pm 0,77$ мг/100 г. У зразках сорту Карамоза загальний вміст антоціанів знизився з $46,93 \pm 2,34$ до $20,41 \pm 1,02$ і до $34,59 \pm 1,72$ мг на 100 г плодів у контрольних і оброблених зразках відповідно. Загальні фенольні сполуки (ЗФС) у контрольних зразках сорту Вікторія спочатку складала $129,86 \pm 6,49$ мг/100г, а в кінці експерименту знизилася до $111,15 \pm 5,55$ мг/100 г, у той час як у досліджуваному зразку ЗФС залишалися незмінними. ЗФС в Карамоза спочатку були на 40% більше, ніж у Вікторії, тобто складала $181,51 \pm 9,07$ мг/100 г. Після 13 діб зберігання ЗФС зменшувалися до $131,00 \pm 6,55$ та до $150,2 \pm 7,50$ мг/100 г у контрольних та оброблених зразках відповідно. Вплив обробки був статистично та практично значущим. Під час зберігання антиоксидантна активність плодів зменшувалася поступово. Зміна антиоксидантної активності оброблених зразків була менш значною, ніж у необробленому зразку, тобто на 17,9 та 23,3% для плодів сортів Вікторія та Камароза відповідно. Основним антоціаніном у плодах обох сортів був пеларгонідин-3-О-глюкозид. Його початковий вміст у плодах становив $68,45 \pm 3,42$ і $65,28 \pm 3,26\%$ від загальної кількості антоціанів для сортів Вікторії та Камароза відповідно.

Висновок. Обробка фруктів суниці за допомогою комбінованих розчинів метилжасмонату, саліцилової кислоти та аскорбінової кислоти позитивно вплинула на зберігання плодів. Вмісту антоціанів та загальних фенолів, а також антиоксидантного потенціалу протягом періоду зберігання було значно підвищено.

Оброблення комбінованим розчином призвело до поліпшення текстури плодів під час процесу зберігання.

Ключові слова: *полуниця, фенол, антиоксидант, антоціан, метилжасмонат, саліцилова кислота, аскорбінова кислота.*

Формування функціонально-технологічних властивостей фаршів з яловичини з використанням харчової добавки на основі нанопорошку подвійного оксиду дво- та тривалентного заліза

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Вступ. Досліджено вплив харчової добавки на основі нанопорошку подвійного оксиду дво- та тривалентного заліза на показники якості й технологічні властивості м'ясних фаршів з яловичини.

Матеріали і методи. М'ясні фарші з яловичини, в які додавали нанопорошок подвійного оксиду дво- та тривалентного заліза у кількості 0,05 – 0,15 %. Волого- та жируотримувальну здатність визначали за допомогою жироміра та рефрактометра; стійкість фаршевих емульсій – методом центрифугування; ступінь penetрації та граничне напруження зсуву – на конусному пластомірі; липкість – за величиною зусилля розділення двох поверхонь, зв'язаних фаршем.

Результати і обговорення. За рахунок великого питомого об'єму, спорідненості до білків, бактеріостатичності, високого хімічного потенціалу і термостабільності нанопорошок подвійного оксиду дво- та тривалентного заліза має сорбційні, комплексоутворюючі, емульгуючі, вологозв'язуючі, водо- і жируотримувальні властивості. Тому сприяє формуванню нових функціонально-технологічних показників м'ясних фаршевих систем і покращенню споживчих характеристик одержаних з них готових виробів.

Введення харчової добавки на основі нанопорошку подвійного оксиду дво- та тривалентного заліза у фарші з яловичини у кількості 0,05–0,15% до маси м'яса сприяє покращенню органолептичних (на 1,0–1,2 бала за 9-бальною шкалою) та функціонально-технологічних показників порівняно з контролем: вологоутримувальна здатність збільшується на 1,1–2,0%; жируотримувальна здатність – на 1,2–2,6%; емульгуюча здатність – на 1,3–2,0%; стабільність або стійкість фаршевих емульсій – на 1,4–2,1%. Також сприяє зменшенню рівня загального мікробного забруднення з $6,2 \times 10^5$ КУО/г – у контролі до $(5,1–5,8) \times 10^5$ КУО/г у зразках, збагачених Fe_3O_4 , тобто на 6,5–19,6%. Втрати при термообробці дослідних зразків охолоджених фаршів з додаванням 0,05–0,15% Fe_3O_4 зменшуються на 14,4–18,4 %.

Раціональна кількість харчової добавки на основі нанопорошку подвійного оксиду дво- та тривалентного заліза – 0,1% до маси м'ясної сировини.

Висновки. Харчова добавка на основі нанопорошку подвійного оксиду дво- та тривалентного заліза покращує якість і технологічні характеристики м'ясних фаршевих систем.

Ключові слова: *м'ясо, фарш, оксид заліза, якість.*

Хімічний склад листя гуньби сінної

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Вступ. Досліджено хімічний склад листків гуньби сінної, яка є джерелом біологічно-активних речовин і використовується як пряно-ароматична сировина в кондитерських виробках.

Матеріали і методи. Дослідження хімічного складу проводили методами: ультрашвидкісної високоєфективної рідинної хроматографії; спектроскопії; газової хроматографії з мас-селективним детектуванням. Для дослідження складу агліконів екстрактів листя було використано кислотний гідроліз. Після проведення гідролізу, аглікони екстрагували етиацетатом, екстракти використовували для хроматографічного аналізу. Для ідентифікації компонентного складу було використано метод дериватизації.

Результати і обговорення. У складі листків гуньби сінної підтверджено наявність фенольних сполук, фенолкарбонових кислот, хлорофілу, алкалоїду тригонеліну, які мають високий антиоксидантний потенціал. З літературних джерел відомо, що фенольні сполуки у рослинах рідко зустрічаються у вільному стані. Більшість їх представлено у вигляді різноманітних О- і С-глікозидів. Різноманіття флавоноїдних глікозидів обумовлено значним набором цукрів і можливостями присднання їх як агліконів, а також тим, що цукри можуть мати різну конфігурацію глікозидних зв'язків. У процесі досліджень ідентифіковані: луксоза, бета-dl-арабінопіраноза, сукроза (цукроза), рафіноза, гліцерин, ксилітол. Доведено наявність амінокислот: L-аланіну, L-валіну, L-проліну, L-треоніну. Ідентифіковані також оксооцтова кислота; сукцинова кислота; 2, 3-діоксипропанова кислота; 2, 3, 4-тригідроксимасляна кислота; пальмітинова кислота; альфа-ліноленова кислота.

Ефірна олія гуньби містить: гексадецен, ейкосанол, етилпальмінат, етиллинолат; ліноленову, бета-гідроксимасляну, бета-амінізомаляну, гідроксибутандикарбонову, 1, 2, 3-пропантрикарбонову кислоти; етилові ефіри ліноленової, леулінової, пальмітинової, етилпальмітинової, лимонної кислот, які, ймовірно, формують флейвор пряно-ароматичної сировини.

Висновки. Наявність у листках гуньби фенольних сполук, есенціальних нутрієнтів, ароматичних речовин має сприяти подовженню терміну придатності, підвищенню харчової цінності, поліпшенню органолептичних властивостей кондитерських виробів.

Ключові слова: гуньба сінна, листя, прянощі, аромат, фенол.

Зміна холестерину та вміст вільних жирних кислот у сирі Карс Грейвер (турецький молочний продукт, вироблений традиційним способом)

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Вступ. Проведено дослідження змін співвідношення вільних жирних кислот та холестерину в сирі Карс Грейвер, виготовленому у традиційний спосіб, залежно від

тривалості дозрівання, а також жирнокислотного складу і рівня холестерину залежно від тривалості дозрівання сиру.

Матеріали і методи. Вміст жиру у зразках сиру визначали методом Гербера. Для ідентифікації окремих жирних кислот і визначення вмісту холестерину використовували хроматографію з пламенево-іонізаційним детектуванням (GC/FID).

Результати і обговорення. Встановлено, що вміст жиру у зразках сиру Карс Гравієр становить 27,0–38,50%. Масова частка холестерину в зразках сиру коливається від 45,70 до 55,80 мг/100 г під час дозрівання протягом 90 днів. У зразках сиру Карса Грав'єра виявлено 16 насичених і ненасичених жирних кислот. Також було зазначено, що у зразках сиру Грав'єра вміст летких жирних кислот (жирні кислоти та міристинової кислоти) збільшується до 25-го дня ($P < 0,01$) і зменшується з 45-го дня до 90-го дня. Вміст вільних жирних кислот (пальмітинова і лінолева кислоти) загалом зменшуються до 25-го дня, а потім знову починає збільшуватися і зростає до кінця періоду дозрівання. Після 90 днів зберігання сиру Карса Грав'єра вміст пальмітинової, олеїнової, міристичної та стеаринової кислот становить близько 74,29% від загальної кількості вільних жирних кислот. У досліджуваних зразках основними насиченими жирними кислотами є пальмітинова та стеаринова кислоти. Було показано, що олеїнова кислота - домінуюча ненасичена жирна кислота. У зразках сиру вміст мононенасичених жирних кислот (MUFA) і поліненасичених жирних кислот (PUFA) становить 28,38–32,37% і 1,59–1,84%, відповідно. Для зразка сиру Карса Грав'єра індекс атерогенності (AI) становить 2,57–3,04.

Висновок. Жирні кислоти є попередниками ароматичних сполук, таких як вільні леткі жирні кислоти з коротким і середнім ланцюгом, а також етикетони, етери та тіоетери, що утворюються в сирі внаслідок перебігу різноманітних біохімічних процесів. Наявність значної кількості жирних кислот з короткими та середніми ланцюгами є причиною аромату сиру Грав'єр.

Ключові слова: *сир, груєр, холестерин, жирні кислоти.*

Ідентифікація бджолиного воску та його фальсифікату методом інфрачервоної спектроскопії

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Вступ. Визначення спектральних особливостей природного бджолиного воску методами інфрачервоної (ІЧ) спектроскопії відбивання та поглинання з метою виявлення наявності вуглеводневих домішок, зокрема парафіну та церезину.

Матеріали та методи. Натуральний бджолиний віск, парафін, церезин, а також їх суміші досліджувалися методом інфрачервоної спектроскопії відбивання та поглинання за допомогою спектрометрів Infracord-61, Luminar 5030 та SPECORD M-80.

Результати та обговорення. Інфрачервоні спектри відбивання від гладких поверхонь зразків (парафін, церезин, віск, суміш бджолиного воску та церезину, суміш воску парафіну та церезину, суміш воску та парафіну) мають подібну

структуру. Спостерігаються два явно виражені максимуми на довжинах хвиль 1510 та 1581 нм. Співвідношення $R_{w(1581)}/R_{w(1510)}$ змінюється у діапазоні від 1,115 до 1,265. Найменше значення відповідає натуральному бджолиному воску, а максимальне значення – церезину. Після подрібнення зразка інфрачервоні спектри дифузного відбивання не зазнали суттєвих змін, найбільш інтенсивні спектральні максимуми не змінили свого положення, але відбувся перерозподіл спектральних ліній за інтенсивністю. Чітко виражені відмінності в області від 1723 до 2400 нм. Коефіцієнт α для спектрів відбивання від гладкої поверхні становив $\sim 1,2$, а для спектрів відбивання від подрібнених зразків $\sim 1,1$. Відмінності спектрів відбивання в області спектра від 1100 до 1350 нм проявляються на довжині хвилі 1212,5 нм.

Спектри ІЧ-спектра дали змогу з'ясувати різницю між природним бджолиним воском і церезином через співвідношення характеристик відбиття при 1510 та 1581 нм: максимальне відношення відповідало воску, а найменше відношення – церезину. Різні пропорції смуг, що відповідають валентним коливанням CH_2 та CH_3 , показали, що вуглеводневі ланцюжки молекул воску довші, ніж молекули досліджуваних парафіну та церезину. Встановлено, що вуглеводневі домішки в бджолиному воску асоціюються із звуженням смуги $\text{C}=\text{O}$ при $\sim 1736 \text{ cm}^{-1}$.

Висновки. Виявлені спектральні закономірності дадуть змогу ідентифікувати натуральний бджолиний віск і виявити його фальсифікат.

Ключові слова: *віск, парафін, церезин, спектроскопія, фальсифікат.*

Протимікробні властивості модельних препаратів у системній концепції здоров'я

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Вступ. Ми проаналізували протимікробну ефективність досліджуваних препаратів серії КТІОЛ-БФ на стандартних культурах мікроорганізмів: *S. aureus*, *Escherichia coli*, *P. aeruginosa* та *S. saprophyticus*.

Матеріали та методи. Досліджуються модельні препарати серії КТІОЛ-БФ (біологічно функціональні). Препарати створені на основі рослинних і тваринних екстрактів, що містять розчин йоду або не містять його. Як контроль використано препарати повідон-йод та хлорофіліпт. Протимікробні властивості зразків препаратів визначили за модифікованим методом дифузії ("стінний" метод) щодо збільшення верхнього діапазону оцінювання.

Результати і обговорення. Науковим підґрунтям дослідження є системна концепція здоров'я, що розроблена на основі еколого-технологічної системи КТІОЛ-I і фізіологічно функціональної системи КТІОЛ-II. Препарат на основі рослинного екстракту забезпечив початковий хороший протимікробний ефект на всі досліджувані мікроорганізми. Введення до препарату на основі екстрактів рослин і на основі рослинних та тваринних екстрактів з розчином нанорозмірних часток колоїдного срібла до 35 мас. % трохи зменшило протимікробну дію зразків щодо *S. aureus* і *S. Saprophyticus*. Зразок на основі рослинних і тваринних екстрактів показав гарний протимікробний ефект на мікроорганізми *S. Saprophyticus*, *E. coli*, *P.*

aeruginosa. Зразки показали хороший протимікробний ефект на всі досліджувані мікроорганізми.

Модельні зразки препарату на основі двофазних рослинних модифікованих екстрактів забезпечили дуже добру інтегральну протимікробну дію на всі досліджувані мікроорганізми. Із них два зразки на основі екстрактів рослин та на основі рослинних і тваринних екстрактів виявили високу протимікробну дію на штам кишкової палички (діаметр затримки росту 30 мм).

Підтверджена можливість високої антимікробної дії на штам *E. coli* (затримка зростання діаметра 30 мм). Це пов'язано з комплексною дією цих двох зразків на досліджувані грампозитивні і грамнегативні штами мікроорганізмів.

Висновки. Виявлена та підтверджена можливість високої протимікробної активності зразків на основі двофазного рослинного екстракту та на основі рослинного екстракту і розчину йоду на штам *Escherichia coli*. Ті ж самі зразки показали високу та хорошу протимікробні властивості як на інших штаммах, так і інтегрально.

Ключові слова: *КТЮЛ, мікроорганізм, резистентність, E. coli, антимікробний, здоров'я.*

Дослідження функціонально-технологічних властивостей білкового композиту тваринного походження

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Вступ. Метою дослідження є вивчення функціональних і технологічних властивостей отриманих білкових композицій із м'яса птиці та визначення оптимальної з високими показниками якості.

Матеріали і методи. Досліджується м'ясо механічного обвалювання птиці, філейна частина птиці, окорок із шкурою, яке піддавалося мікрохвильовому вакуумному сушінню з вологістю не більше 5%, готові зразки Мерго 85 (голландського виробника) – тваринні білки великої рогатої худоби та Sunprotein – рослинний білок.

Результати і обговорення Отримані результати свідчать про те, що отримані сухі порошки дають змогу наблизити готовий продукт до продукту зі збалансованим складом, високої якості і харчової цінності. Досліджено, що зразки з філейної частини, окорок курячий та м'ясо механічного обвалювання містили більше вільної вологи 80-96%, що надає продукту з його використанням більшої соковитості і ніжної консистенції.

При цьому найкраща водоутримувальна здатність у зразка з філейної частини 10,2% та у Sunprotein – 11,4%. Найбільшу жирутримувальну здатність мало м'ясо механічного обвалювання птиці – 13,1%, якщо порівняти із зразком Мерго 85 – 5,25%. Емульсійна здатність у зразку м'ясо механічного обвалювання птиці становить 73%, що на 20–25% вище порівняно з іншими зразками.

У результаті проведення мікробіологічних досліджень не було виявлено бактерій групи кишкової палички, патогенних мікроорганізмів, в тому числі роду *Сальмонела*, сульфїтредукуючих клостридій. Загальна кількість мікроорганізмів після сушіння у всіх зразках не перевищує норматив для вареного сушеного м'яса (5×10^3). Найкращий результат порівняно з іншими спостерігався у зразку Sunprotein – $1,8 \times 10^3$.

При сенсорному аналізі встановлено, що зразок із філейної частини має кращий зовнішній вигляд і запах, тоді як у м'яса механічного обвалювання консистенція краща. Вона найбільш розсипчаста, притаманна сухим порошкам.

Висновки. Порівняльний аналіз підтверджує високі функціональні й технологічні властивості зразків із філейної частини птиці і м'яса механічного обвалювання птиці, а також є безпечними при застосуванні у м'ясних продуктах.

Ключові слова: м'ясо, білок, птиця, добавка, сушіння.

Біотеннологія, мікробіологія

Визначення, характеристика і промислова утилізація автохтонних штамів *Streptococcus thermophilus*, виділених з молдовського сирого молока і молочних продуктів спонтанного бродіння

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Вступ. Молочнокислі бактерії з відомими метаболічними властивостями визначають сенсорні характеристики продуктів, забезпечують їх якість і безпеку. Обмежена кількість високобіотехнологічно доступних штамів і постійний ризик нападів бактеріофагових атак виправдовують необхідність нових штамів.

Матеріали і методи. Визначення термофільних молочнокислих бактерій здійснювалось на основі фенотипічних властивостей і використанням молекулярних методів – RAPD-ПЛР та ФТРП-спектроскопії. Антагоністична активність відібраних штамів проводилася дифузійним методом. Порівняння стартерної культури та зразків йогурту виконувалося за традиційними технологіями.

Результати і обговорення. Вибрані штами *S. thermophilus* характеризуються інтенсивним підкисленням молока протягом 3-4 годин, розвиваючи молочну кислотність 65-74 °Т та утворюючи однорідний компактний щільний коагул, що забезпечує його тверду консистенцію. Штами *S. thermophilus* штамів CNMN-LB-50 і CNMN-LB-51 здатні синтезувати екзополісахариди (ЕПС).

Антагоністична активність протипатогенних мікроорганізмів штамів Росії висока. Діапазон інгібуції від 16 до 18 мм від *Escherichia coli*. і 19-21 мм на *Staphylococcus aureus*, який пригнічує розвиток кишкових інфекцій і запобігає розвитку патогенів у зразках ферментованого молока. Максимальний сигнал EPS, синтезований за субоптимальної температури 32 °С, на 19,4% вище, ніж за оптимальної температури для цього процесу (40 °С) для штамів *S. thermophilus* CNMN-LB-50 і 23,8% для *S. thermophilus* CNMN-LB-51. Щоб стимулювати синтез ЕПС у промислових умовах виробництва кисломолочних продуктів без зміни температури, поживне середовище повинно бути доповнене сахарозою у кількості 8%.

Висновки. Продемонстровано можливість отримання з мікрофлори сирого молока і молочних продуктів спонтанного бродіння автохтонних штамів молочнокислих бактерій з цінними біотехнологічними властивостями, призначених для використання в складі заквасок для виробництва ферментованих молочних продуктів.

Ключові слова: *Streptococcus thermophilus*, молоко, бродіння, ідентифікація.

Харчова безпека

Оцінка концентрації важких металів у їстівних риб'ячих м'язах та зразках води, зібраних з різних локацій біля Читтагонгу: проблема охорони здоров'я

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Вступ. Проведено дослідження концентрації важких металів у зразках риби та води, зібраних із різних районів Читтагонгського району, Бангладеш.

Матеріали та методи. Концентрації важких металів, включаючи Cr, Cu, Ni, Pb та Fe у морській воді та морських рибах (пам-крокер, бомбейська качка і анчоус) виявлені за допомогою атомно-абсорбційного спектрометра у районі міста Читтагонг, Бангладеш.

Результати та обговорення. Середня концентрація важких металів була виявлена у воді в діапазоні Cr 0,01338-0,0789 мг/л, Cu 0,0014-0,0284 мг/л, Ni 0,0259-0,2519 мг/л, Pb 0,0109-0,1596 мг/л, і Fe 0,2176-1,787 мг/л. Аналіз зразків води показав, що розподіл важких металів в порядку величини, виглядає так: Fe > Ni > Pb > Cr > Cu. Різниця може бути пов'язана з розташуванням локацій, рівнем забруднення у воді через промислові стоки та антропогенні види діяльності. Хоча середня концентрація важких металів була виявлена у всіх зразках риби в діапазоні Cr 3.2039-16.3495 мг/кг сухої маси, Cu 1.5589-4.5848 мг/кг сухої маси, Ni 0.1101-1.9029 мг/кг сухої маси, Pb 0.4373-2.7638 мг/кг сухої маси і Fe 30,9599-108,780 мг/кг сухої маси. Розподіл важких металів у зразках риби виглядає так: Fe > Cr > Cu > Pb > Ni. Аналіз показав, що величини важких металів були більш-менш схожі з даними інших дослідників. Різниця може бути пов'язана із накопиченням металів у рибі та різноманітних видах риб, що живуть у одній водоймі, але різного рівня забруднення у воді. Серед усіх зразків 17% зразків риби мали надлишок Cr, в той час як прийнятна межа дорівнює 15.0 мг/кг для риб. Середні концентрації Pb у всіх рибних зразках були на 17% нижче рівня виявлення, 33% – оптимальні та 33% – вищі, ніж максимально дозволені концентрації (1,5 мг/кг). Fe у всіх рибних зразках був на 33% нижчим, 17% – оптимальним і 50% – вищим, ніж максимально дозволені концентрації (43 мг/кг), рекомендовані ФАО/ВООЗ.

Висновки. Більшість досліджених видів риб є безпечними для споживання. Тому це дослідження спрямоване привернути увагу органів охорони здоров'я та охорони навколишнього середовища до потреб відповідної регуляторної бази.

Ключові слова: важкий метал, вода, море, морська риба, Читтагонг.

Процеси і обладнання

Інтенсифікація охолодження рукавних полімерних пакувальних плівок стічною плівкою рідини

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Вступ. Проведено аналітичні й натурні дослідження процесу охолодження пакувальної плівки з поліетилену високого тиску (ПЕВТ) стічною водяною плівкою.

Матеріали і методи. Експериментальні дослідження охолодження плівки проведені за таких параметрів: тип плівки – плоска; швидкість руху плівки – 0,03–0,50 м/с; розміри щілинного розподільника водяної плівки: величина щілини – 0,4–0,8 мм, ширина щілини – 300 мм; температура охолодної води – 15–40 °С. Рациональні параметри процесу охолодження визначені на основі математичного моделювання.

Результати і обговорення. Параметри рідинної плівки змінюються тільки на вхідній ділянці й залежать від щільності зрошення, швидкості полімерного рукава й початкового розподілу швидкості плівки рідини на виході з розподільного кільця. За високих значень щільності зрошення ($Re > 20000$) у теплообміні бере участь лише пристінний шар рідини.

Для плівки з поліетилену високого тиску її зовнішня поверхня твердне на відстані близько 0,01 м від початку контакту з водою, а внутрішня поверхня – на відстані близько 0,10–0,15 м. Тому кільце для розподілу рідини необхідно встановлювати після закінчення ділянки роздуву заготовки полімерного рукава. Також потрібно забезпечити стійкий рух суцільної плівки рідини по зовнішній поверхні полімерного рукава на довжині до 0,2 м від початку контакту рідини з полімерною плівкою.

Температура охолодної води в діапазоні 20–60 °С істотно не впливає як на інтенсивність процесу охолодження, так і на фізико-механічні властивості одержуваної полімерної плівки.

Для товстих плівок з ПЕВТ (завтовшки понад 200 мкм) і завширшки понад 1 м інтенсивність охолодження обмежена критичною щільністю зрошення.

Для практичного застосування отриманих результатів запропоновано номограму для визначення об'ємної щільності зрошення охолодної води, а також об'ємної продуктивності технологічної лінії залежно від розмірів готового полімерного рукава.

Висновки. Наукове значення результатів полягає у визначенні раціональних умов застосування рідинного охолодження одержуваних екструзією рукавних полімерних плівок.

Ключові слова: *упаковка, полімер, екструзія, плівка, охолодження.*

Вплив нанорозмірного гідроксиду алюмінію на структурно-механічні властивості бурякової тканини

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Вступ. Проведені дослідження з метою підтвердження доцільності використання нанорозмірного гідроксиду алюмінію в процесі екстрагування сахарози з бурякової стружки з метою підвищення структурно-механічних властивостей бурякової тканини.

Матеріали і методи. Дослідження термохімічного впливу водних розчинів додаткових реагентів на структурно-механічні властивості бурякової тканини методом гідравлічного пресування зразків тканини цукрового буряка циліндричної форми із заданими геометричними розмірами. Перед цим кожен з отриманих зразків підлягав тепловій обробці у водних розчинах різних реагентів при температурі 70–72 °С і тривалості досліду 60 хв.

Результати та обговорення. Обробка зразків бурякової тканини додатковими розчинами сульфату алюмінію, сульфату кальцію, нанорозмірного гідроксиду алюмінію та їх комбінаціями в процесі екстрагування при температурі 70–72 °С дасть змогу зменшити ступінь деформації зразків бурякової тканини порівняно зі зразком, що не піддавався обробці додатковими реагентами. Ступінь зростання бурякової тканини, що був оброблений розчином нанорозмірного гідроксиду алюмінію, на 18 % нижчий, ніж контрольний зразок без обробки додатковими реагентами. Такий результат можна пояснити високою хімічною активністю реагенту нанорозмірного гідроксиду алюмінію. Іони цієї сполуки здатні утворювати в поверхневому шарі тканини досить стійкі нерозчинні комплексні сполуки з пектиновими і білковими речовинами, які, адсорбуючись на шарі бурякової тканини, формують щось подібне до молекулярного каркасу, що підвищує стійкість бурякової тканини до стискаючих навантажень.

Величиною, яка найточніше може описати якість бурякової тканини, є її здатність відновлювати свою форму та пружність при періодичних стискаючих навантаженнях, є саме: модуль пружності. При тепловій обробці за температури 70–72 °С модуль пружності зразків бурякової тканини, що піддавалася обробці додатковим реагентами, на 35-40% вищий, ніж зразок бурякової тканини без обробки додатковими реагентами.

Висновки. Застосування в процесі екстрагування нанорозмірного гідроксиду алюмінію, забезпечить збереження цілісності структури бурякової тканини в процесах екстрагування та пресування; гарантує високу якість екстрагенту, дифузійного та очищеного соку.

Ключові слова: цукровий буряк, стружка, тканина, екстрагування, нанорозмірний, гідроксид алюмінію, пружність.

Крутильні коливання гвинтового робочого органу шнекового багатofункціонального транспортера з урахуванням динаміки суцільного потоку оброблювального середовища

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Вступ. Метою статті є математична модель коливань робочого органу шнекового транспортера для транспортування сипких вантажів з урахуванням зміни щільності оброблюваного середовища, швидкості обертання шнека, маси при появі явища резонансу.

Матеріали і методи. Досліджуються крутильні коливання гвинтового робочого органу шнекового багатofункціонального транспортера, які виникають внаслідок дії оброблювального середовища. Дослідження проведено методом математичного моделювання.

Результати і обговорення. Основними обмежуючими факторами, які ускладнюють моделювання, є нерівномірність розподілу середовища уздовж довжини шнека; тіло виконує гнучкі коливання; рух оброблюваного середовища вздовж робочого гвинта спричиняє малі коливання згину, викликає появу «додаткових сил». Для забезпечення достовірності математичної моделі введено такі припущення: робочий гвинт шнека обертається з постійною кутовою швидкістю навколо своєї поздовжньої осі, яка в недеформованому положенні збігається з віссю OX; вектором визначається поперечне переміщення нейтральної осі робочого гвинта у довільному моменті в напрямку, перпендикулярному його недеформованому положенню (щодо фіксованої системи відліку OXYZ); безперервний потік обробленого середовища, маса якого на одиницю довжини повільно змінюється вздовж гвинта і рухається з постійною відносною (відносно робочого шнека) швидкістю.

Математична модель враховує обмеження і припущення для існуючого шнекового транспортера довжиною 2,5 і 3 м, який використовується для переміщення сипких вантажів щільністю 10, 20, 40 кг/м. Змінними параметрами є довжина шнека, щільність оброблюваного середовища, швидкість обертання шнека, маса.

На основі моделі побудовано залежності амплітуди коливань від довжини шнека, щільності оброблюваного середовища, швидкості обертання шнека, маси.

Висновки. Математична модель дає змогу удосконалити процес розробки і проектування шнекових транспортерів сипких вантажів, забезпечуючи при цьому надійність процесу транспортування та системи «оброблюване середовище–гвинтовий робочий орган».

Ключові слова: шнек, конвеєр, амплітуда, резонанс, моделювання.

Автоматизація технологічних процесів

Ефективна робастно-оптимальна система керування пластинчастою пастеризаційно-охолоджувальною установкою в умовах дії інтенсивних зовнішніх збурень

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Вступ. Досліджено робастно-оптимальну систему керування пастеризаційно-охолоджувальною установкою, що функціонує в умовах інтенсивних зовнішніх збурень, інформаційної та структурної невизначеності, з метою підвищення ефективності її функціонування.

Матеріали і методи. Методи системного аналізу, математичної статистики та ідентифікації використовуються для побудови математичної моделі об'єкта керування. Для синтезу робастно-оптимального регулятора застосовано 2-Ріккати підхід для проблеми H_2 -керування, а для зменшення порядку отриманого регулятора – метод збалансованого зменшення моделі.

Результати і обговорення. Пастеризаційна установка є ключовим компонентом виробництва молочної продукції. Оскільки результати роботи традиційних автоматизованих систем залежать від інтенсивності та якості інформаційних потоків, мікропроцесорної техніки, алгоритмічного та програмного забезпечення, пропонується доповнити їх робастно-оптимальним регулятором на основі 2-Ріккати підходу. На основі визначеної математичної моделі об'єкта, що складається з лінійних диференціальних рівнянь сьомого порядку, синтезовано робастно-оптимальний регулятор 6-го порядку. Показники ефективності розраховуються шляхом порівняння синтезованої системи та системи з локальними регуляторами. У робастно-оптимальній системі розмах невизначеності збільшився в чотири рази, а дисперсія керуючих сигналів зменшилася в чотири рази, що підтверджує енергоефективність системи.

Висновок. Проведене моделювання та розрахунок якісних характеристик показали значну перевагу синтезованої системи перед системами з локальними регуляторами.

Ключові слова: робастний, оптимальний, 2-Ріккати, невизначеність, H_2 -регулятор.

Економіка і управління

Представлення інтересів сільськогосподарських виробників: обґрунтування структури дослідження

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Вступ. Метою статті є обґрунтування структури наукових досліджень, яка дає змогу оцінити участь сільськогосподарських виробників у процесах формування аграрної політики держави.

Матеріали і методи. Під час дослідження використовувалися методи наукового обґрунтування, аналізу, систематизації, синтезу та опитування. Теоретичне обґрунтування базується на аналізі теорій управління, що пояснює характер міжорганізаційної взаємодії.

Результати і обговорення. Представляти інтересів сільськогосподарських товаровиробників у процесі формування аграрної політики є недоцільним. Як приклад для дослідження ми вибрали Литву і встановили, що 85,6% сільськогосподарських виробників не є членами асоціацій чи об'єднань і тільки близько 10% з них беруть участь у роботі сільськогосподарських організацій.

Результати дослідження показують, що відповідно до політики фінансової підтримки агропідприємств у ЄС проблема участі зацікавлених осіб в управлінні підприємством зменшує можливість великих і малих сільськогосподарських виробників захищати свої інтереси. Програма участі та спільного управління і концепція партнерської та міжорганізаційної взаємодії були узгоджені шляхом:

- а) відмежування відповідних груп асоціацій сільськогосподарських виробників від участі в процесі формуванні політики галузі;
- б) розроблення схеми для досягнення балансу між потребами зацікавлених осіб та асоціацій сільськогосподарських виробників;
- в) формування теоретичної бази для подальшого якісного опитування всіх учасників взаємовідносин.

Під час аналізу результатів досліджень було встановлено, що досягнення інтересів, заснованих на потребах, повинне стати головним завданням для політиків. Для цього необхідно забезпечити збалансованість впливу зацікавлених сторін з метою врахування інтересів усіх учасників. Результати досліджень показують, що з метою досягнення інтересів зацікавлених осіб потрібно враховувати їхні потреби в процесі формування агрополітики товаровиробника.

Висновок. Сформована у дослідження система дає змогу систематично збирати якісні дані та подавати раціональні пропозиції політичним і сільськогосподарським організаціям.

Ключові слова: *сільське господарство, фермер, управління.*

Instructions for authors



Dear colleagues!

The Editorial Board of scientific periodical
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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
 - ReferencesIf 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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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.
2. **Назва статті.**
3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озеряно).
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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 - Висновки
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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 Journal взято 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.

Всі елементи посилання розділяються комами.

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.

Посилання на електронний ресурс:

Виконується аналогічно посиланню на книгу або статтю. Після оформлення даних про публікацію пишуться слова **Available at:** та вказується електронна адреса.

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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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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