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Contents

Phytochemical composition of *Helichrysum arenarium* (L.) Moench essential oil (aerial parts) from Turkey

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Abstract

Introduction. The aim of the present study was to determine the phytochemical composition of *Helichrysum arenarium* (L.) Moench (aerial parts) essential oil and extracts obtained from Turkey as a source of bioactive components for the food, cosmetics and pharmaceutical industry.

Materials and methods. The flower essential oil was obtained by hydrodistillation for 2 h and its composition was analyzed using gas chromatographic analysis (GC/MS). Extracts were obtained from the air-dried flowers by treatment with 70 and 90% ethanol (1:5 v/w) in an ultrasonic bath. In the extracts, the total phenolic content was obtained by Folin-Cicalteu method. The total flavonoid content was determined by $Al(NO_3)_3$ reagents, measured at wavelength 415 nm against a blank. Antioxidant activity of the extracts was determined using DPPH, ABTS, FRAP, and CUPRAC assay.

Results and discussion. The amount of extracted essential oil was 0.07% with the main constituents oleic acid (30.28%), ethyl hexadecanoate (20.19%), linoleic acid (18.89%), and sclareol (4.22%). The composition of the oil predominated by oxygenated hydrocarbons (76.90%), followed by diterpenes (11.50%), hydrocarbons (3.53%)), oxygenated sesquiterpenes (3.30%), phenyl propanoids (2.93%), sesquiterpene hydrocarbons (1.43%), monoterpene hydrocarbons (0.34%), and oxygenated monoterpenes (0.07%). The content of the total polyphenols in the 95% ethanol extracts was 7.56 mg GAE/g dw and the total flavonoids was 3.13 mg GAE/g dw, whereas their content in the 70% ethanol extract were 6.62 mg GAE/g dw and 3.34 mg GAE/g dw, respectively. Among the plant samples, 70% ethanol extract exhibited higher CUPRAC (159.46 mM TE/g dw) followed by ABTS radical action decolourization (47.53 mM TE/g dw). The results for ethanol extracts and their antioxidant activity were in accordance with the total phenolic content and the concentration of flavonoids. The flowers of *H. arenarium* were dominated by total carotenoid (10.68 μg/g dw), followed by total chlorophyll (51.24 μg/g dw). The content of chlorophyll a (32.67 μg/g dw) was higher than that of chlorophyll b (18.57 μg/g dw).

Conclusions. The main compounds of the *H. arenarium* essential oil were oleic acid, ethyl hexadecanoate, linoleic acid, and sclareol. The extracts showed a high level of total phenolic content and antioxidant potential, which make the studied plant species as a potential source of alternative natural antioxidant or a source of biologically active components.

Introduction

Helichrysum arenarium L., commonly known as immortelle or everlasting among the population, is a plant with a pronounced potential for use and application in various spheres of life. The immortelle belongs to the genus *Helichrysum* (*Asteraceae* family) and includes over 600 species in the world. The genus is represented also in Turkish flora by 27 taxa (21 species and 6 subspecies), and 15 of them are endemic [1].

Due to the wide range of application of the plant, in some regions of the Turkey the plant was cultivated for the purpose of industrial production of essential oil, for use in cosmetics and food industry.

The species is widely used for essential oil isolation, because the oil have economic and pharmaceutical importance as they are used as a plant preservative [2]. The majority of authors confirm that the therapeutical effect of plants is attributed mainly to the presence of flavonoids and polyphenols [3].

In Turkey, the plant has been used only in folk medicine [1], which is a prerequisite for its cultivation for use in other sectors such as food, pharmacy and cosmetics industry.

The literature contains data on the chemical composition of the essential oil obtained from plants growing in different countries of Europe and Asia.

Radusiene and Judzentiene [4] isolated the essential oil from the differently colored (citric-yellow, citric, yellow, orange, yellow-brown and brown) inflorescences of *H. arenarium* growing in Lithuania. *Trans*-caryophyllene (8.8%), δ-cadinene (8.2%), and 1,8–cineole (7.0%) were the major constituents in essential oils from citric inflorescences. The oil from brown inflorescences contained *trans*-caryophyllene (7.8%), whereas tetradecanoic acid (7.0%) was the major constituents of oils from yellow and yellow-brown inflorescences. The main constituents of *H. arenarium* essential oil from China were sesquiterpenes β-spatulenol (19.9–24.03%), ledol (6.22–10.02%), bicyclogermacrene (5.68%), aromadendrene (5.15%), and α-eudesmol (4.29–4.37%) [5]. The chemical composition of *H. arenarium* essential oil from Hungary was represented by linalool (1.7%), anethole (3.2%), carvacrol (3.6%), and α-muurolene (1.3%) [6].

The analysis of the data showed that the chemical composition of the essential oil was different, which depends on both the method of its obtaining and the soil and climatic conditions of growing the plant.

The *H. arenarium* essential oil demonstrated antimicrobial activity [7, 8] against various microorganisms, including pathogenic strains. Other authors, such as Tepe *et al.* [9] reported the antioxidant activity of the methanol extracts of four Turkish *Helichrysum* species.

Although the immprtelle plant was extensively investigated in different parts of the world, there were no data in the literature for the determination of secondary metabolites (pigments chlorophyll and carotenoids, essential oil, phenolic compounds and flavonoids) in the flowers of *H. arenarium* growing in Turkey, as well as for the antioxidant activity of its ethanolic extracts.

Therefore, the aim of this study was to determine the phytochemical composition of *Helichrysum arenarium* (L.) Moench (aerial parts) essential oil and extracts obtained from Turkey as a source of bioactive components for the food, cosmetics and pharmaceutical industry.

Materials and methods

Plant material

The aerial parts of *H. arenarium* were collected in full flowering stage on 31 July 2018 from Yozgat Akdagmadeni district (39°34.647' N 35°48.568' E, altitude 1760 m). Then dried at room temperature (18±2 °C) and relative humidity of 65% for 14 days. The samples were packed in plastic bags and stored at 23±2 °C until being abalyzed.

Isolation of essential oil

The moisture of the flowers (9.91%±0.09) was determined by drying up to constant weight at 105 °C [10].

The air-dried flowers were cut to a size of 0.5 mm. The essential oil was isolated by hydrodistillation for 2 h in a laboratory glass apparatus of the British Pharmacopoeia [11]. The oil obtained was dried over anhydrous sodium sulfate and stored in tightly closed dark vials at 4 °C until analysis.

Chemical composition of essential oil

The GC analysis was performed using a GC Agilent 7890A, an HP-5 ms column (30 m x 250 μm x 0.25 μm), temperature: 35 °C/3 min, 5 °C/min to 250 °C for 3 min, total: 49 min; helium as a carrier gas at 1mL/min constant speed, and 30:1 split ratio.

The GC/MS analysis was carried out on an Agilent 5975C mass spectrometer, using helium as a carrier gas, and the same column and temperature as in the GC analysis.

The identification of chemical compounds was done by comparison to their relative retention time and library data. The identified constituents were arranged in order of retention time and quantity in percentage.

Ultrasound-assisted extraction

The ultrasound-assisted extraction of biologically active substances from air-dried flowers was performed in an ultrasonic bath SIEL UST 5.7–150, Gabrovo, Bulgaria, with frequency 35 kHz and 300 W. The extraction procedure was performed with two solvents with different polarity 95% and 70% ethanol in the ratio (1:5 v/w). The dried plant materials were weighed in a 50 mL centrifuge tube with a screw cap and then 20 mL solvent was added to the sample. The tubes were placed in the ultrasonic bath at 55 °C for 20 min. The ultrasound-assisted extraction was performed in triplicate. Each extract was filtered and the combined extracts were used for further analysis.

Total phenolic content

The total phenolic content (TPC) was determined using the Folin–Ciocalteu reagent [12], as the extract (0.2 mL) was mixed with 1 mL Folin–Ciocalteu reagent diluted (1:5) and 0.8 mL 7.5% sodium carbonate. After 20 min at room temperature (25 °C) in darkness, the absorption was measured at wavelength 765 nm against a blank sample. [13].

Total flavonoids content

The total flavonoids content was analyzed by Al $(NO_3)_3$ reagents and measured at wavelength 415 nm against a blank [14]. The results were presented as mg quercetin equivalents (QE) per g dw.

Antioxidant activity

The DPPH radical scavenging activities of flowers were evaluated [15], and the absorbance was measured at wavelength 517 nm. Radical scavenging activity of samples was expressed as mM Trolox® equivalent (TE) per g dw.

ABTS radical action decolourization assay

ABTS radical was generated as an aliquot part of 7.0 mM 2,2`azinobis (3)ethylbenzthiazoline-–sulfonic acid (ABTS, Sigma) in distilled water was mixed with 2.45 mM potassium persulfate in distilled water. The reaction was performed for 16 h at ambient temperature (25 °C) in darkness. Before analyses, 2.0 mL of generated ABTS.+ solution was diluted with methanol at proportions 1:30 (v/v), to the final absorbance of the working solution about 1.0 ÷ 1.1 at wavelength 734 nm. $ABTS^{\cdot+}$ solution (2.85 mL) was added to 0.15 mL extracts. After 15 min at 37 °C in darkness, the absorbance was measured at wavelength 734 nm against methanol. The antioxidant activity was expressed as mM TE/g dw [13].

Ferric reducing antioxidant power assay (FRAP)

The FRAP method was performed as previously described [16] and the absorbance was recorded at wavelength 593 nm. The results were expressed as mM Trolox® equivalent per g dw.

Cupric reducing antioxidant capacity (CUPRAC) assay

One mL $CuCl_2 \times 2H_2O$, 1 mL Neocuproine (7.5 mL in methanol), 0.1 M ammonium acetate buffer (1 mL), 0.1 mL extracts and 1 mL distilled water was mixed. The reaction was performed for 20 min at 50 °C in darkness. After cooling the absorbance was measured at wavelength 450 nm. The antioxidant activity was expressed as mM TE/g dw [13].

Total Chlorophylls and Carotenoid content

For determination of chlorophyll a, chlorophyll b, total chlorophylls and the total carotenoids, the absorbance of 95% ethanol extracts was measured at three wavelengths 664 nm, 648 nm, and 470 nm. The amount of these pigments was calculated according to the formulas (–4), [17].

$$\text{Chlorophyll a (Ca)} = 13.36A_{664.2} - 5.19A_{648.6} \quad (1)$$

$$\text{Chlorophyll b (Cb)} = 27.43A_{648.6} - 8.12A_{664.2} \quad (2)$$

$$\text{Total Chlorophyll (a+b)} = 5.24A_{664.2} + 22.24A_{648.6} \quad (3)$$

$$\text{Total carotenoids} = [1000A_{470} - 2.13C_a - 97.64C_b]/209 \quad (4)$$

Results and discussion

Chemical composition of essential oil

In our study, the essential oil content (yield) was 0.07% ± 0.00 in the plants. The chemical composition of *H. arenarium* essential oil was presented in Table 1.

In the essential oil, 42 constituents representing 97.89% of the total content were identified. Ten of them were in concentrations over 1% and the rest 32 constituents were in concentrations under 1%. The main constituents in the plant essential oil (above 3%) were: oleic acid (30.28%), ethyl hexadecanoate (20.19%), linoleic acid (18.89%), and sclareol (4.22%).

The main components' groups were found to be oxygenated hydrocarbons (oleic acid, ethyl hexadecanoate, and linoleic acid), followed by diterpenes (scraleol), hydrocarbons (n-tetracosane), oxygenated sesquiterpenes (cedrol), phenylpropanoids (carvacrol), sesquiterpene hydrocarbons, monoterpene hydrocarbons, and oxygenated monoterpenes.

The chemical composition of *H. arenarium* essential oil was previously studied by several researchers [18, 19, 20]. In their paper, Leonardi et al. [18] analyzed essential oils obtained from six species of *H. arenarium* growing in Italy. One hundred seventeen components were identified representing 90.1–98.5% of the total chemical composition, mainly characterized by sesquiterpenes and monoterpene compounds. Judzentiene and Butkiene [19] studied the essential oil composition of *H. arenarium* of leaves and inflorescences of different colors from natural populations from eastern Lithuania. It was found that the principal constituents were *β*-caryophyllene (in three inflorescences and one leaf oil), *δ*-cadinene (in two leaf samples), octadecane (in one leaf sample) and heneicosane (in one inflorescence sample). Later, in 2019, Judzentiene et al. [20] investigated the chemical composition of the 16 essential oils obtained by hydrodistillation from inflorescences and leaves of *H. arenarium* plants growing in Lithuanian forests. Similarly to the data reported by Leonardi et al. [18], they determined that the main fractions were found to be sesquiterpenes (29.0–70.1%) and aliphatics hydrocarbons (7.7–45.5%). It is also reported that *β*-caryophyllene, *δ*-cadinene, and octadecane, were among the main constituent of *H. arenarium* essential oil collected in Lithuania. Different species of *Helichrysum* showed significant differences in chromatographic profiles. The results reported by Juliano et al. [21] showed that the chemical composition of *H. microphyllum* subsp. *tyrrhenicum* essential oil s collected in four different regions in South-Western Sardinia, was represented by a significant amount of neryl acetate, *γ*-curcumene, and linalool. Kurkcuoglu et al. [22] reported a study for the chemical composition, simultaneously analyzed by GC/FID and GC/MS obtained by the aerial parts of *H. noeanum* Boiss. and *H. chionophilum* Boiss. et Balansa. They reported that the main constituents were identified as hexadecanoic acid, dodecanoic acid, tetradecanoic acid, and decanoic acid. Besides the specificity of studied species the differences between the essential oil composition in this study and that from other studies, reported in the literature, are probably due to the climatic conditions in the respective location where the plants were grown, and also to the plant parts processed and obtained.

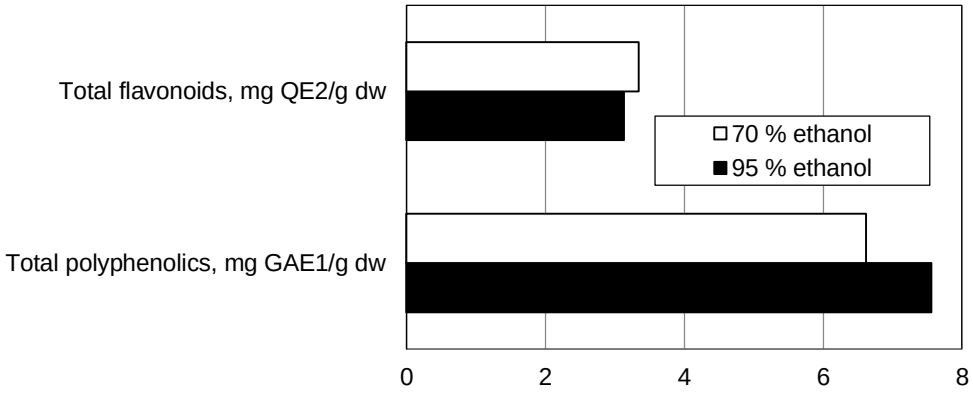
Table 1

Chemical composition of the *H. arenarium* essential oil

№	Name	RI	Content, %
1.	*α*-Pinene	932	0.10 ± 0.0
2.	*p*-Cymene	1019	0.08 ± 0.0
3.	*γ*-Terpinene	1054	0.07 ± 0.0
4.	*β*-Linalool	1095	0.07 ± 0.0
5.	Borneol	1165	0.10 ± 0.0
6.	n-Dodecane	1200	0.06 ± 0.0
7.	Thymol	1289	0.11 ± 0.0
8.	Carvacrol	1297	2.68 ± 0.02
9.	β-Caryophyllene	1417	0.56 ± 0.0
10.	Aromadendrene	1439	0.17 ± 0.0
11.	*α*-Caryophyllene	1453	0.13 ± 0.0
12.	Germacrene D	1484	0.11 ± 0.0
13.	*γ*-Cadinene	1513	0.23 ± 0.0
14.	*δ*-Cadinene	1522	0.20 ± 0.0
15.	(2E)-Tridecenol	1568	0.10 ± 0.0
16.	Spathulenol	1576	0.15 ± 0.0
17.	Caryophyllene oxide	1582	0.13 ± 0.0
18.	Viridiflorol	1591	0.21 ± 0.0
19.	Cedrol	1600	0.67 ± 0.0
20.	*β*-Cedren-9-one	1632	0.08 ± 0.0
21.	epi-α-Cadinol	1640	0.48 ± 0.0
22.	*α*-Cadinol	1653	0.20 ± 0.0
23.	7-epi-α-Eudesmol	1662	0.32 ± 0.0
24.	*α*-Bisabolol	1685	0.10 ± 0.0
25.	Cedroxyde	1713	0.14 ± 0.0
26.	Methyl tetradecanoate	1722	2.79 ± 0.02
27.	(2E,6E)-Farnesyl acetate	1844	0.31 ± 0.0
28.	n-Nonadecane	1900	0.26 ± 0.0
29.	Methyl hexadecanoate	1922	2.54 ± 0.02
30.	Phytol	1943	0.20 ± 0.0
31.	Sclarene	1974	0.30 ± 0.0
32.	Ethyl hexadecanoate	1997	20.19 ± 0.19
33.	n-Eicosane	2000	0.16 ± 0.0
34.	n-Heneicosane	2100	0.18 ± 0.0
35.	Methyl octadecanoate	2124	0.48 ± 0.0
36.	Linoleic acid	2132	18.89 ± 0.17
37.	Oleic acid	2141	30.28 ± 0.29
38.	Sclareol	2222	4.22 ± 0.04
39.	3α-hydroxy-Manool	2301	0.67 ± 0.0
40.	3α-14,15-dihydro-Manool oxide	2337	2.89 ± 0.02
41.	3α-acetoxy-Manool	2362	2.98 ± 0.02
42.	n-Tetracosane	2400	2.86 ± 0.02
	Hydrocarbons, %		3.53
	Oxygenated hydrocarbons, %		76.90
	Monoterpene hydrocarbons, %		0.34
	Oxygenated monoterpenes, %		0.07
	Sesquiterpene hydrocarbons, %		1.43
	Oxygenated sesquiterpenes, %		3.30
	Phenyl propanoids, %		2.93
	Diterpenes, %		11.50

Total phenolic and flavonoid content

The results for total phenolic and flavonoids content of *H. arenarium* extracts are shown in Figure 1. The total phenolic content of the 95% ethanol extracts was higher (7.56 ± 0.08 mg GAE/g dw) than the other sample. On the other hand, the amount of flavonoids for 70% ethanol was greater (3.34±0.15 QE/g dw) than that of 95% ethanol extract. Our results for 70% ethanol extracts were lower than the results obtained by Babota et al. [23] for the phenolic content (25.17 mg GAE/g dw) and total flavonoid content (27.17 QE/g dw). In a study performed by Albayrak et al. [24] the TPC value ranged from 71.81 to 125.57 mg GAE/g of methanolic extracts of two subspecies of *H. arenarium* from Turkey.



*[1]GAE - Gallic Acid Equivalents, [2]QE - Quercetins Equivalents

Figure 1. Total polyphenolics and flavonoids content of *H. arenarium* extracts.

Antioxidant activity

The antioxidant activity of *H. arenarium* extracts, determined via four methods (DPPH, ABTS, FRAP, and CUPRAC) was presented in Figure 2. The anti-radical activity of the samples with 70% ethanol displayed higher values than the samples with 95% ethanol by the methods of ABTS and CUPRAC.

Our results were higher than that reported by Babota et al. [23] who determined the antioxidant activity of 70% ethanol extracts of *H. arenarium* against the stable synthetic ABTS radical action (5.82±0.02 mM TE/g/dw) and the method of DPPH (17.88±7.20 mM TE/g/dw). Albayrak et al. [24] reported lower values for antioxidant activity (23.03 mM TE/g/dw and 47.64 mM TE/g/dw) determined by the method of DPPH for two subspecies of *H. arenarium* from Turkey.

The results for ethanol extracts and their antioxidant activity were in accordance with the total phenolic content and the concentration of flavonoids.

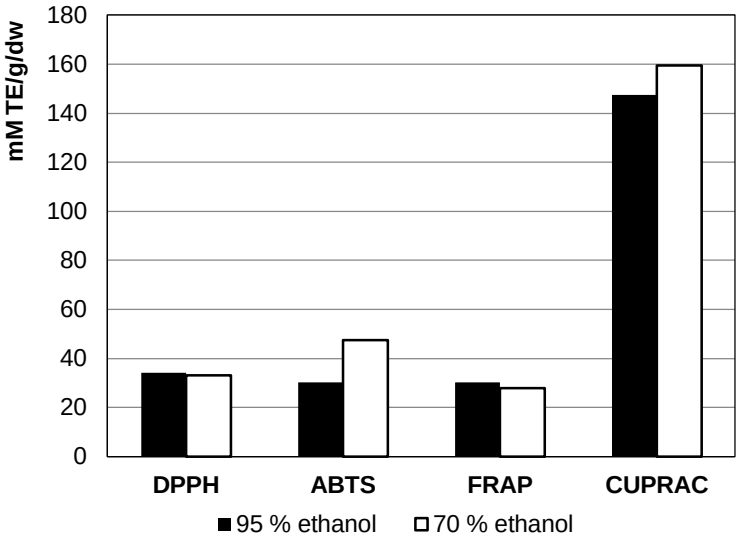


Figure 2. Antioxidant activity of *H. arenarium* extracts

Total Chlorophylls and Carotenoid Content

The chlorophyll and carotenoid contents in the analysed samples were presented in Table 2. Ethanol is a solvent that dissolves both polar (hydrophilic) and non-polar (hydrophobic/lipophilic) substances. The results showed that the total chlorophyll content predominated in the composition of the sample, followed by carotenoid content.

Table 2

Content of pigments in the dry raw material of *H. arenarium*, µg/g dw

H. arenarium	Chlorophyll a	Chlorophyll b	Total Chlorophyll	Total Carotenoid
	32.67±0.21	18.57±0.08	51.24±0.24	10.68±0.11

According to previous reports [17], the number of porphyrin pigments varied depending on environmental conditions, high-temperature inversions, lack of water and minerals. Higher levels of chlorophyll a (32.67%) than those of chlorophyll b (18.57%) could be a marker of the presence of contamination [25] in both the soil layers and the air where the samples were collected. The extraction method of carotenoids was similar to that of chlorophylls, as they are part of the photosynthetic pigments in plant cells. The values of total chlorophylls and carotenoids in the tested samples may vary depending on the type of solvent used [17], its polarity and the conditions of their extraction. Changes in the content of chlorophyll pigments were a typical abiotic stress associated primarily with induced aging, light stress, nitrogen deficiency and others, in which initially the content of chlorophyll a decreased stronger than chlorophyll b.

Conclusions

1. The qualitative composition of the obtained essential oil from *H. arenarium* from Turkey demonstrated the content of volatile biologically active components with potential for use in the food, cosmetics and pharmaceutical industry,
2. The ethanol extracts from *H. arenarium* from Turkey exhibited pronounced antioxidant properties based on high levels of flavonoids, polyphenols and porphyrin pigments.

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Improving the quality of soybean by-products by physical methods during its use in bakery technology. Review

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Abstract

Introduction. Secondary raw materials of soybean processing (SMSP) have a high nutritional value, but its use in food is limited by a rough taste and a low content of soluble dietary fiber.

Material and methods. The subject of the study is the properties of SMSP, soluble dietary fiber, trypsin inhibitor, physical methods of raw materials processing, bakery products, and pastries. Research methods are analysis and synthesis of information of the world's leading scientific publications.

Result and discussion. Based on the analysis of research results it was determined that there is an influence of physical factors of SMSP processing on their nutritional value, technological and consumer features of finished products. Therefore, the relevance and perspective of the use of physical factors are proved. High pressure significantly affects soluble dietary fiber and functional features of legumes' wastes. At 400 MPa and 60 ℃ under high pressure, the content of soluble dietary fiber increases by 8 times during SMSP treatment in comparison to the untreated one. Swelling and water (oil) retention features are improved. After ultrafine grinding SMSP has improved technological indicators. Their use in baking leads to improved organoleptic characteristics. Ultrafine grinding improved the physical and chemical indicators of SMSP (viscosity, cation exchange capacity, ability to retain water and oil, solubility, hydration features, fluidity, antioxidant activity), technological indicators (test formability, the stability of its structure), organoleptic parameters. Microwave treatment has a strong penetration power. The electromagnetic wave leads to the increasing of pressure in the cell of material, its expansion, and rupture. It also leads to an increase in soluble dietary fiber content in SMSP. Microwave treatment is an effective way to inactivate the activity of a protease inhibitor in soybean cracks. Only two minutes roasting reduces the activity of the trypsin inhibitor to 13.33% from the initial one.

Conclusion. The use of physical methods combination of SMSP quality improvement is promising. Ultrafine grinding of SMSP has advantages in comparison to other physical methods. It affects significantly on physical, chemical, technological features and the quality of bakery products and pastries.

Contents

Introduction

China is a main producer of soybean products and the cultivation and processing industry of beans has a long history. The main products of soybean production include soybean milk and tofu, and the by-product of soybean milk production is soybean dregs [1]. Based on the vigorous development of China's soybean industry, the soybean food industry can produce tens of thousands of tons of wet bean dregs each year, with a residue up to 70%. The development of soybeans has brought great economic benefits to the food industry, which can produce 15 million tons bean dregs per year [2–4]. Soybean residue is rich in nutrients, containing 50% dietary fiber, 25% protein, 10% fat, 33% isoflavones, slightly higher amino acid content than soy milk, as well as calcium, phosphorus, iron and B vitamins. Therefore, bean dregs have the nutritional characteristics of high fiber, high protein, low fat and low reducing sugar, and is rich in mineral elements of potassium, calcium and magnesium et al [5–8]. The texture of bean dregs was similar to that of copra, Japanese like to add bean dregs into soup, salad and vegetables. It was obvious that bean dregs had good potential as a functional food material [9]. Bean dregs had a certain health care function and was a good dietary fiber raw material [10–17] (Table 1).

Generally, the development and use of bean dregs are more common in feed mills and food processing, or directly burned as waste, which causes certain economic losses [5] . In the food, it can be used in bakery products [18–20], noodles [21–23], and steamed bread [24]. At present, the dietary fiber products produced by deep processing of bean dregs had the disadvantages of high water content, poor taste, easy spoilage, and low soluble dietary fiber (14%), and contains some ant-nutritional factors, which had a great impact on the health of people or animals for a long time [25]. Therefore, to improve the added value of bean dregs in food was not only to increase the content of dietary fiber, but also to elimination of ant-nutrient factors in bean dregs, which is related to human health and safety.

Table 1

Main nutrition composition of products of soybean (g/100 g dry matter) (%)

Alias	Dietary fiber	Protein	Lipid	Reference
Bean dregs	52.8–58.1	25.4–28.4	9.3–10.9	[13]
Soy pulp	42.4	15.2	8.3	[14]
Bean curd dregs	49	33.4	19.8	[15]
Okara	54.3	33.4	8.5	[16]
Soybean residue	53.25	24.21	9.83	[17]

The content of soluble dietary fiber and the taste and quality of bean dregs can be improved by different processing technologies. A large number of studies show that the soluble dietary fiber of bean dregs can be improved by with physical technology. Such as novel blasting extrusion processing [26], steam explosion [27], electrohydrodynamic [28], and high pressure [29]. The application of these physical techniques also increases the soluble dietary fiber of other raw materials, such as that extrusion technology increased dietary fiber on cereals [30]. Ultrafine grinding technology can effectively improve the functional properties of the b-products of grain, provide the delicate taste for the product [31], this new technology has been proven and used to prepare ultrafine powders with good properties [32]. High pressure as a new technology and gradually applied to the b-products of grain, and has made great progress and contributions, at the same time, high pressure inactivated about 90% trypsin inhibitors [33]. Several efforts have been made by researchers to exploit the bean dregs and improve the quality of baked goods in the production of highly nutritious food products.

The content of soluble dietary fiber and the taste and quality of bean dregs can be improved by different processing technologies. Nowadays, ultrafine grinding technology can effectively improve the functional properties of bean dregs dietary fiber, which not only improves the utilization of soybean resources but also conductive to environmental protection. Ultrafine powder was the final product of ultrafine grinding, and has special physical and chemical properties not available in general particles, such as good solubility, dispersibility, adsorption, chemical reactivity and the like. Ultrafine powder has been widely used in many fields such as food, chemical, pharmaceutical, cosmetic pesticides, dyes, coatings, electronics and aerospace. In recent years, high pressure as a new technology in the food industry usually used in meat products, vegetables, drinks, jam, and a small part of grain products, and more in basic research.

This review compiles the research carried out on functional characteristics and utilization of dietary fiber of bean dregs in baked goods (bread, cake and biscuit). The effects of physical techniques on quality improvement of bean dregs were reviewed. In this review, we aim to highlight physical methods impact on bean dregs and baked goods are emphasized, as well as the effects of physical techniques on anti-nutrition factors. Further research should focus on technological innovations to develop high quality raw materials from soybean b-products to improve the quality of baked foods.

1. Dietary fiber

1.1. Physiological functions of dietary fiber

Dietary fiber is the general term of the carbohydrates that are not easy or cannot be decomposed and digested by digestive enzymes and absorbed of human intestinal tracts after being ingested by human, including cellulose, hemicellulose, lignin, pectin, mucus, gum, β-glucan, arabinoxylan and so on. It was resistant to digestion and adsorption in the human small intestine and can be fully or partially fermented in the large intestine [34, 35]. With the development of society and the continuous improvement of human living standards, people had less intake of dietary fiber, and food nutrition has not been properly matched. In the long run, it will cause diseases such as diabetes and obesity. Dietary fiber intake requirements (25g for women and 38g men every day) [36]. Dietary fiber can affect the ecology of human intestinal microorganisms, promote intestinal peristalsis, increase satiety, lower blood glucose levels, and also has the effect of losing weight [37, 38]. The presence of dietary fiber may change the gelatinization temperature, molecular structure and crystallite structure of the starch, thereby further affect the digestive properties of the food. Daily intake of dietary fiber can reduce hunger, prolong food intake, and control cholesterol intake [39]. Dietary fiber can effectively inhibit the growth of harmful bacteria, promote the proliferation of beneficial bacteria, regulate the balance function of intestinal flora, and protect colonic health [40]. With the development of nutrition and related disciplines, more and more studies had found that dietary fiber plays a very important role in human health. It was an indispensable nutrient for human healthy diet, especially in the health of the digestive tract. Comprehensively, dietary fiber has physiological functions, such as lower blood fat and blood sugar, improve the intestinal environment, and control body weight [41, 42]. The bean dregs dietary fiber was mainly composed of cellulose, hemicellulose (dry weight content 40~60 g/100 g) and lignin. Dietary fiber includes soluble and insoluble dietary fiber. However soluble dietary fiber has a potential "prebiotic" label [43, 44]. Soluble dietary fiber has high viscosity and strong water holding capacity. It can be used by intestinal microorganisms and slow down the digestion rate. And delay the body's absorption of water compounds by carbon bodies, play a part in reducing postprandial blood glucose, and improve insulin sensitivity [45]. Dietary fiber includes soluble and insoluble dietary fiber. Soluble dietary fiber consists of naturally formed gels or viscous fibers such as hemicellulose, seaweed polysaccharides, guar gum, pectin, et al [46]. Soluble dietary fiber can reduce the mechanisms of postpranational blood sugar, for example, slowing the digestion of food in the stomach [47], antagonistic glucagon [48], inhibit the absorption of glucose in the small intestine [49]. Insoluble dietary fiber cellulose mainly contains cellulose and hemicellulose, which can promote gastrointestinal motility, accelerate food absorption through the gastrointestinal tract, reduce energy absorption, and clean the digestive wall, dilute carcinogens in food, and accelerate the migration of toxic metabolites [50, 51]. In addition, it is good for intestinal health and prevention of colon cancer.

There are a lot of foods containing dietary fiber, such as grains, vegetables, fruits, tea and other processed of scraps, and many wastes from food factory also containing large amount of dietary fiber, such as wheat bran, rice bran, yam skin, dragon skin, navel orange peel, tea stems and so on. Add dietary fiber to cereal products, not only can increase nutrition, prevents disease, but also improve the viscosity, texture, sensory properties of the product, and extend the shelf life of the food. Therefore, recycling and reusing waste resources not only enriches food types, but also increases the added value of products, which is of great practical significance.

1.2. Application of different types of fibers in bakery products

Different types of fibers were used in baked products to effectively improve the viscosity, texture, and sensory properties of the product, while reduced the heat of the product [52, 53]. It increases the nutrition and flavor of the product and better meets the consumer's demand for high dietary fiber food. Microwave reaction technology is combined with ultrafine grinding was used to separate the dietary fiber from the cardamom, and used in the production and development of biscuits. The results showed that the hardness of the biscuit product improved with the increase of cardamom dietary fiber content. Addition of 10% cardamom dietary fiber was used instead of wheat flour. The biscuit has anti-free radical properties, and was 6 times higher than that of the control group. Above 7.5% cardamom dietary fiber addition, the nutritional and quality properties of the biscuit improved [54]. Used jet mill to treat barley and rye flour for biscuit production, the composite flour was softer than the commercial flour, the color was darker, and the total phenolic content and antioxidant activity were higher, and barley flour was increased in hardness compared to biscuits made from whole wheat flour. Rye flour was darker in color, so the biscuits were darker in color [55]. Used bean powder and soy protein powder to make biscuits. Soybean protein powder has a higher protein content of 9.42% compared with that of wheat flour. The addition of soybean powder improved the nutritional quality of biscuits, and further increases the sensory score of biscuits [56]. By optimizing the formulation of the biscuits, the resistant starch 14%, sodium caseinate 14.51%, raftilose 25%, and simplesse 25.02%, a lo-sugar, low-fat "functional" biscuit was developed. Add to sodium caseinate can increase the hardness of the biscuit dough, and the thickness of the biscuit was positively correlated with the texture [57].

When making biscuits, by adding different types of dietary fiber, the sensory properties of the product can be improved, and the calories of the biscuits can be reduced, thereby becomes a functional food that is beneficial to the human body. For the addition of fiber, although the nutritional value of the product is improved, whether the taste and texture of the biscuits meet the needs of consumers, and whether the cost is accepted by the producer, we need to do further research. There are many foods contained fiber. The bean dregs were wastes in soybean processed. The bean dregs were mostly used in feed mills or discarded, which caused waste of resources. In order to further increase the added value of products, a large number of studies have proved that bean dregs highly utilized in food, and mostly used for the development of flour products. In recent years, in recent years, many varieties of bean dregs have been developed, such as taro, bread, biscuits, cakes, noodles, etc. The addition of bean dregs complements the nutritional value of the products, and increased the overall acceptability of the product. And bean dregs Not only develops new varieties, but also a new market has been developed.

2. Application of bean dregs in baked goods

With the development of the food industry, the availability of bean dregs has been gradually developed, and commonly used in baked goods (cakes, bread, biscuits). Addition the bean dregs in the flour and adds the correspond ingredients to make the bean dregs biscuits, it not only improved the flavor of the traditional biscuits, but also provided a new type of healthy food for consumers. A large number of literature studied has shown that the addition of bean dregs to flour. It can improve the nutrition and flavor of biscuits, and provided a new method for the utilization of soybean food [58, 59].

2.1. Application of bean dregs in bread and cakes

Bean dregs can be used in a variety of Wester-styles baked goods, it not only to provide natural fiber and protein, but also to provide a unique fragile texture for bread, muffins, donuts, brownies, marshmallows, etc [60]. The bean dregs bread was made from the bean dregs and the flour, assess the sensory, texture, and flavor of bread products. With the increased of the amount of bean dregs, the bean flavor of the bread was more intense. The hardness was gradually increased, and the internal texture was superior to ordinary bread. Above 10% level bean dregs powder, the bread was soft, with aroma, and the highest quality score. However, hardness, cohesiveness and occlusion of the bean dregs bread were higher, and the elasticity was lower, which provided a reference for the improvement of the bean dregs bread [61]. The used of bean dregs and grain rice to mix and make puffed biscuits, the rice cake made by mixing the ratio of bean dregs, and rice flour to 7:3 was most popular among the public. The addition of bean dregs was related to moisture and hardness, and the heating temperature and time were affected specific area of rice cake. The higher the content of bean dregs, the greater the hardness, the smaller the specific volume area and the lower the integrity. The bean dregs fiber was combined with rice flour, increased the adhesion strength between the particles and the toughness of the biscuit. With the increased of the amount of bean dregs, the L^* value and the a^* value of the product gradually decreased, and the b^* values increased significantly [62]. Make a new type of cake product, used eggs, flour, sugar, bean dregs and peanut dregs as raw materials. Among them, flour: peanut residue: bean dregs were (1:1:3), The finished cake was complete in shape, attractive in color and aroma, and the finished product is soft and elastic. The pores were evenly distributed and the flavor was outstanding. The total dietary fiber content was 3.1%, and better than traditional cake. Nevertheless, there is a fishy smell in bean dregs or peanut dregs, how to use a certain technology to effectively remove, and still need to be further research [63]. The mixture of bean dregs and rice flour is used to make glute-free layered cakes. The addition of bean dregs has a great impact on the cake batter and the product. When the substitution percentage of rice four by bean dregs increased the decrease in cake volume is observed, giving rise to harder and less cohesive cakes. When addition 10% of the bean dregs flour can improve the quality and nutrition of the cake [64]. When making bean dregs bread, based on wet bean dregs, sugar, yeast, butter, the dough was analyzed and the bread was sensory evaluated. In the test of dough, the decisive indicators were hardness, elasticity and chewability. The sensory evaluation of bread was related to the dough, and chewability does not have much effect on dough quality [65]. When making bean dregs bread, added 8% bean dregs can increase the water absorption properties of bread flour, and improve the stretching properties of the dough. Addition of bean dregs increased the hardness and chewability of bread, and delays the aging rate of bread [66]. The soybean cake was fermented in stages, which shorten the fermentation process. As the increased of fermentation time, the hardness of the bean dregs cakes increased significantly, and the elasticity, cohesiveness and resilience decreased significantly. The surface of bean dregs cake had obvious changes, the inside of the product occurred uniform air holes, and organization more uniform [67].

A large number of literature have shown that bean dregs were added to bread can increase the nutritional value of the product, improve the flavor and volume of the product, and also have the effect of delaying aging. However, due to the strong water absorption of the bean dregs, a large amount of the addition will increase the hardness of the product, and the elasticity, cohesiveness and recovery were reduced, thereby affecting the taste of the product. These studies can provide more reference for the improvement of the bean dregs bread. Soybeans have a certain taste of soybean meal, and directly affect the taste quality of the product. The reason was that the oxidization of fat oxidase in soybean causes the oil to

oxidize, thereby produce the taste of soybean meal. Bean curd in the bean dregs also exists, and whether it will affect the flavor of the product and other series of problems, and it should be paid close attention.

2.2. Application of bean dregs in biscuits

Biscuits as a widely consumed product in the world, it has rich nutritional value and become an indispensable snack food [68, 69]. Biscuits are baked goods with lower water activity than bread. Biscuits usually made from wheat flour, eggs, sugar, salt, oil and water [70]. Biscuits play an important role in the baked industry, the main factors affected the quality of biscuits was the texture, taste and appearance of biscuits. Improve the nutritional content of cookies and being accepted by consumers is the most important aspect [71, 72]. The word "biscuit" comes from France, it means r-baked bread, the earliest biscuits were baked from bread. The biscuits were mainly divided into tough biscuits, crisp biscuits and fermented biscuits on the market in China. The crispy biscuits were made of lo-gluten wheat flour as the main raw material, with more oil and sugar, and the taste was crisp. The dough of the plastic biscuit lacks elongation and elasticity, it has good plasticity, the biscuit is crispy and sweet, it is a highly acceptable biscuit variety. The tough biscuits are a kind of biscuit with less sugar and fat, it is composed of wheat flour, sugar (or suga-free) and oil as the main raw materials, and added leavening agent, modifier, and other auxiliary materials. After the process of powdering, rolling, forming, baking. The surface of the biscuit had many patterns, the appearance was smooth and flat, there was even pores, the section was layered, and the taste was crisp. Biscuits have become a kind of snack food instead of people's lives, because of different tastes and textures, it was suitable for all the people. With the improvement of living standards, a new generation of mea-making biscuits on the market, which can control calories, it is the main ingredient for obese patients to lose weight. Bean dregs have rich in dietary fiber, among them, insoluble dietary fiber content is high. However, the taste of the bean dregs is not easy to be accepted by the public. Therefore, the development of functional food has been done by researchers.

Mix fresh bean dregs with starch, soy flour, and hydroxypropyl methylcellulose to make biscuits. Among them, the highest water retention of the dough with hydroxypropyl methylcellulose was 147.8%. Bean dregs dough has the lowest elasticity, followed by soya flour dough. Soy flour crackers and hydroxypropyl methylcellulose crackers were harder during storage. Bean biscuits were crispy and chewy. However, fresh bean dregs may produce a fishy smell and may affect the shelf life of the finished product [73]. The amount of bean dregs added directly affects the performance of the biscuit dough, and the taste of the finished product, on the basis of adjusting the amount of oil, sugar and water added, the maximum amount of the bean dregs powder was 40%. The greater the amount of bean dregs added, will affect the formation of biscuits, but it may require the addition of more grease [74]. The bean dregs were rich in dietary fiber, and the bean dregs were retreated with ultrafine grinding used to make cookies. With butter, bean dregs powder, sugar powder and baking process as a single factor, through orthogonal experiments, determine the best process recipe for making bean dregs biscuits: flour 864g, bean dregs powder 180g, 300g sugar powder, 750g butter, baking temperature was 180 °C, bottom fire 160 °C, baked time 12 min. Under this formula, the biscuit has golden color and the shape to keep good, crispy taste and rich bean flavor. There were more bean dregs added, which was a kind of hig-fiber snack food, it suitable for most consumers, and included special people, it can improve human health to a certain extent [75]. The use of ultr-fine powdered bean dregs to produce suga-free bean dregs biscuits, and the quality of the products from the shape, texture, taste, aroma and color of the biscuits to determine the best process conditions for making biscuits: baked

temperature 160 °C, baked time 10 min, the bean dregs addition amount was 30%, the oil: sugar mass ratio was 1.0:1.5, the oil and sugar: the optimal ratio of the bean dregs flour was 1.0:2.0, and the ratio of baking soda to ammonium bicarbonate was 2:1. It is shown that the addition of bean dregs can increase the content of wet gluten in the flour. When the amount of bean dregs added was less than 7.5%. The rheological properties of the dough were good, which was beneficial to the formation of biscuits [59]. Untreated bean dregs were directly added to wheat flour for the development of crisp biscuits, the best optimized formula was obtained: bean dregs: Wheat flour were 3:7, butter was added in 30% of powder, and sugar was added in 20% of powder, baked temperature: 200°C on fire and 180°C under fire, the biscuit has a complete structure, uniform color and crispy taste, it has rich aroma of bean dregs and good quality [76]. But whether biscuits produced with wet bean dregs will reduce the shelf life of the biscuits, and whether the taste was better than the biscuits made from dried bean dregs. The addition of wet bean dregs will cause ant-nutritional factors in the biscuits, which were not conducive to the health of the human body. In addition to this, added to the bean dregs were not pulverized, which may affect the taste. The use of black bean dregs to make biscuits have a significant effect on the water holding capacity, texture, and senses of ordinary bean dregs. When the added amount is 40%, the hardness of the biscuit is the largest. It may be that the dietary fiber in the black bean dregs and the gluten contents in the dough are diluted, which affects the formation of the gluten network, which causes the biscuits to dry out and increase their hardness. Using headspace soli-phase microextraction gas chromatograph-mass spectrometry, the flavor content of 30% black bean dregs cookies is richer, dietary fiber (58.8±0.481) g/100 g, protein content is (23.8±0.175) g/100 g, fat content It was (8.08±0.121) g/100 g, the amino acid nitrogen content was (0.132±0.012) g/100 g, and the ash content was (3.56±0.078) g/100 g [77].

Bean dregs biscuits were made with bean dregs powder, fat, white sugar, and skimmed milk powder as single factors. Through orthogonal tests, sensory evaluation and hardness were the main evaluation indicators. The results showed that the hardness of the biscuit gradually decreased with the increased of the amount of bean dregs, and the hardness was the highest when the additional amount was 20%. The final formula was: flour 88%, bean dregs powder 12%, skim milk powder 20%, fat was 45%, white sugar 40%, egg liquid 35%, baking soda 0.6%, salt 0.6%, the biscuits were golden in color, it has crisp, sweet and milky aroma, it has a certain health effect on the human body [78]. Bean dregs and cassava flour are mixed to produce glute-free biscuits, and inulin is used instead of sugar. Studies have shown that with the increase of bean dregs, the hardness of biscuits increases, color L* value decreases, and the color becomes darker. Using sensory evaluation as the main index, and adding 30% of bean dregs. The quality of the produced biscuits is good. Research under a light microscope revealed no abnormalities in the cookies. The protein and fiber contented of the biscuits has been increased and is welcomed by customers [79]. The addition of the bean dregs, rice bran and broken rice in glute-free sweet biscuits is conducive to improving the stability of biscuits. The experimental sweet biscuits had characteristics of color, weight, volume and diameters (internal and external) very similar to the commercial, whereas texture, lipids and energy value decreased, and water activity, moisture and protein increased during storage. The sweet biscuits showed the same stability when compared to the standard. Thus, the bean dregs, rice bran and broken rice were considered viable alternatives for the development of new products [80]. Bean dregs flour have great potential for application in confectionery products. The formulation of the molded sweet biscuit in which 30 % of the wheat flour was substituted by bean dregs flour was considered adequate. The color, flavor and overall quality of the molded sweet biscuit did not differ significantly from those of the standard biscuits [19].

Researchers have studied the recipe of biscuits, the combination of bean dregs and other powders to make biscuits, it can effectively improve the taste of the product and attractive color. The amount of bean dregs added varies depending on the powder used to carry out the biscuits. For biscuits, the proportion of dietary fiber added to the bean dregs can be increased, because the biscuits have lower requirements for gluten content. However, the sensory evaluation of biscuits has a considerable subjectivity, and different scholars have different opinions on the amount of bean dregs added in biscuits. After the bean dregs were mixed with the flour, the hardness of the product was much increased, and the amount of the bean dregs added was only 10% or less. The combination of bean dregs and starch, bean dregs can be added up to 30%, and will produce a certain degree of brittleness, if it exceeds a certain amount, it may affect the edible taste of the biscuit. There were a wide variety of biscuits, but the above researchers have studied more in bean dregs biscuits, while the research on tough biscuits was relatively rare, especially making recipes for biscuits, most recipes contain more fats and sugars. Although the bean dregs biscuits increased the nutritional needs of human beings to a certain extent, but for special people, whether it can be eaten normally, such a problem deserves our continued discussion. For example, using a certain processing method to treat the bean dregs for the addition of baked goods, so as to develop a functional biscuit suitable for all people to eat, low sugar, low fat, it is a huge challenge currently facing. At the same time, we must control the production process or use some new and improved technologies. In this way, functional food with high quality and nutrition can be obtained. Despite the fact that there are more and more researches on bean dregs, but in the face of existing defects, food workers need to continue to explore, and still require a lot of research work.

2.3. Application of bean dregs in other food

Bean dregs are not only used in baked goods, but also in steamed bread, noodles, dumpling skins and beverages.

Addition bean dregs the water absorption, silty index, formation time and stability time of dough increased and prolong the shelf life of steamed bread [81]. Added to wheat flour at the bean dregs powder of 0, 5, 10, 15 and 20 g/100 g used to make Chinese steamed bread. The results of the present study suggested that increased amount of bean dregs powder led to a significant increase in hardness, gummines, chewiness and adhesiveness in dough and Chinese steamed bread [24]. The ultrafine grinding technology was used to treated bean dregs, and mix flour to make traditional Chinese steamed bread. The quality of steamed bun was the best when the added amount of bean dregs was 13% [82]. Replacing part wheat flour with bean dregs powder to make noodle and steamed bread. Addition to 25% and 15% of bean dregs powder mix with flour to make noodles and steamed bread respectively. Researches show that the noodle and steamed bread had almost similar qualities to those made from 100% wheat flour [83]. Bean dregs may improve rheological properties of silty clay and stretch in certain scope. Addition 16% of bean dregs can improve the rheological characteristics of the flour, and bean dregs noodles reaching the optimum conditions [84]. In addition to, taking bean dregs as raw material, different fungal fermented was used to make bean dregs sauce [85] and white soy Sauce [86].

At present, the bean dregs have been widely used in food, and made a great contribution to the food industry. Domestic and foreign scholars on the research of the bean dregs has not only is still in the primary stage, many researchers use special technology to improve the quality of the bean dregs, applied to food to improve product quality.

3. Application of physical technology in baked goods and cereals

3.1. High pressure

High pressure technology refers to the sealing of food materials in an elastic container or pressur-resistant device system. The pressure conditions are generally (100–700 MPa), it often used water or other fluid medium as a medium to achieve sterilization, and change materials, the purpose of physical and chemical properties. High pressure as a good no-thermal processed technology, it can ensure the safety of food, reduce the process degree of food, and maintain the original flavor of food [87]. High pressure can modify or denature macromolecules (such as starch, protein, etc.) by destroying secondary bonds in macromolecular substances, and small molecules composed of covalent bonds of vitamins, minerals, aroma components and pigments of substance has no significant effect. High pressure technology is commonly used in food processing, and the most mature application is fruit and vegetable processing. For example, used in high pressure technology for the production, sterilization and preservation of fruit and vegetables, jams and juices. High pressure technology also applies to the processing of meat products and aquatic products. For instance, pressure processing shellfish food can not only increase the safety and shelf life of raw meat, but also maintain the fresh taste of shellfish. At the same time, th1e removal of shellfish after high pressure treatment is more convenient. However, high pressure is increasingly used in the processing of food products, such as cereal crops, potato crops and legume crops. At present, the application of high pressure technology in the processing of food products is mainly the modification of starch and protein, such as changing the viscosity and transparency of food, and also relates to the physical and chemical properties relates to food flavor and nutritional value.

As early as 1990, Japan used high pressure treatment products for the first time. Ten years ago in Europe, high pressure processing food were already in the stage of research or trial production, and the label of "new food" was spread throughout Europe [88]. High pressure processing has become a technology with potential use for these purposes. Its main advantages are short processing time, uniform effect, good instantaneity [89]. The comparision with other technologies, such as heat treatment and pasteurization, these techniques fail to maintain the original color, taste and nutrition of the raw materials. While high pressure processing maintains the sensory attributes and nutritional value of the product [90–92]. High pressure processing has become a commercially viable food manufacturing tool. In food processing and preservation applications, the importance of i-situ engineering and thermodynamic properties of food and packaging materials in process design was emphasized [93]. In recent years, high pressure has become a new tool for improving glute-free food, which has changed the properties of food, such as protein and starch [94].

Using high pressure technology to process sugar cookies, research shows that high pressure technology reduces the number of mesophilic bacteria, yeast, and mold microorganisms in the product. After high pressure treatment, the shelf life of biscuit dough is expanded, with a higher density. In the baking process, the maturation time of the biscuit is shortened, compared with untreated dough. Dough processed under high pressure technology corresponds to the biscuit produced, with a darker color, and the dough surface is smooth and uniform. There are even cracks on the surface of the biscuit, but it will not significantly influence the quality characteristics of the biscuit [95]. The cake batter is treated with high pressure technology. When the high pressure condition is 300–600MPa, the duration is 3–6min. Cake paste was measured for microbial flora, density, microstructure and rheology, and the cake was analyzed for specific volume, weight loss, color and

texture. The results showed that compared with the untreated ones, the number of molds and yeast decreased with increasing pressure. The density of the batter increases, the cake volume decreases, the surface color deepens, and the hardness increases [96]. Corn starch and rice flour are respectively subjected to high pressure treatment for bread production. Set the high pressure condition to 600 MPa, 40 C, 5min. The results demonstrate that high pressure treatment can effectively slow down the aging speed of bread, extend the shelf life, and improve bread quality. Therefore, corn starch and rice flour under pressure treatment can increase the shelf life and quality of glute-free bread [97]. Sorghum flour is treated under high pressure for the production and processing of bread. When the pressure conditions at 200–600 MPa, 20 ° C, and observe the rheological properties of the batter. When the pressure at 300 MPa, the batter structure weakens. When the pressure is higher than 300 MPa, the batter consistency increases. At 600 MPa, processing 2% sorghum flour can delay the aging of bread. Adding 10% sorghum flour, the exact volume of the bread is small, and the product quality is poor. Therefore, under appropriate pressure conditions, the amount of sorghum flour should be controlled [98].

High pressure technology has made a great contribution to grain products, changing the performance of grain and improving product quality. Cereals undergo high pressure treatment, which can effectively reduce the amount of microorganisms in food and extend the shelf life of food. After the batter is treated with high pressure, it can effectively improve the rheological properties, the structure of the batter is enhanced, and the color of the product can be increased. But as the pressure increases, the hardness of the dough will gradually increase. On the basis of improving the product, the quality of the product is not covered, so the pressure conditions corresponding to different products are different. Studies have revealed that the high hydrostatic pressure treatment in the heat rheology of batter, with the increased of pressure level, induced gelation of starch content. High pressure treatment at 450 MPa and 600 MPa, 25 C for 15 min, the concentration of gouache paste was (1:5), gelation was completed, the higher concentration of slurry requires higher pressure、temperature or longer holding time [99]. High pressure treatment significantly increases dough hardness and adhesion and reduces stickiness. When making bread, use a scanning electron microscope to observe the cut surface of the bread. Under pressure at 0–200MPa, as the pressure increases, the pores become larger and larger, the protein is affected when the pressure level is higher than 50MPa, and the starch modification requires a higher pressure level. High pressure treatment has little change in the color of the dough, but during the baking process, the color of the breadcrumbs changes dramatically. Studies have shown that high hydrostatic pressure treatment can obtain grain products of the new type in the range of 50–200MPa [100]. Wheat starch slurry (10% w/v) was subjected to high hydrostatic pressure treatment at 300, 400, 500, 600 MPa, 20 °C for 30 minutes. The gelation temperature was lowered, the surface and internal structure particles of the starch were destroyed, and waxy wheat starch was effectively modified [101]. High pressure can change the secondary structure of SPI, 7S, 11S proteins in nanoemulsion. Enhance their stability, and can be used as an effective emulsifier [102]. The gelatinization characteristics of pea starch under high pressure were investigated. At 0–600 MPa, the initial viscosity increased from 8Cp to 34Cp. High pressure treatment can promote "cold gelation" of pea starch aqueous dispersion, and strengthen gelatinization of starch particles. In addition, the shape, size, and particle size distribution of starch particles is changed [103]. Antioxidant activity of buckwheat treated with high pressure was improved. It can also effectively inhibit the formation of fat. After comparison, this study shows that high pressure treatment at room temperature has better nutritional value than no-high pressure treatment [104]. Effects of high pressure and thermal processing on photochemical, color and microbiological quality of herba-plant infusion.

When the high pressure treatment conditions are at 400 or 500 MPa and 25 ° C for 15 or 30 minutes, the natural color of the product can be better retained. The comparison with pasteurization (90 °C, 1–3min). These two treatments can effectively eliminate yeast and *E. coli* [105]. High pressure technology was used to process potato starch, and it for cycles of 6, at 400 MPa, showing higher peak viscosity and attenuation value. For cycles of 3, the peak time and final viscosity was higher than those of the natural control sample. This shows that the treatment under high pressure has a significant effect on the sample. This study can be used to prepare food for slow digestion and hypoglycemia [106]. High pressure treatment can enhance the mixing properties of lo-grade wheat flour in food applications.

When the high pressure conditions are at 500 and 600 MPa, the flour moisture is controlled at 56%, and the starch particles are combined with protein aggregation, which causes the protein network in the dough to break. When the moisture content is 33%, the structure of the dough is promoted, the formation of a protein network and the strength of the dough are increased. At 500 or 600 MPa for 5 minutes, the protein structure is modified and the starch granules remain intact [107]. Taro, carrot and sweet potato are processed under high pressure at 600MPa for 5–30min. The results showed that high pressure treatment caused certain physical damage to the three vegetable structures. It can result in cell wall of vegetables to rupture, increase the drying speed, and shorten the processing time. Reduce gelatinization temperature for sweet potato starch. Increased softening and pr-gelatinization of carrot and sweet potato starch, making it more convenient for consumers to process [108]. The high pressure was used to modify the sweet potato residue, and the microstructure of the insoluble dietary fiber of the sweet potato residue was observed as a loose, smooth, honeycom-shaped porous network structure. The modified insoluble dietary fiber of sweet potato residues has a significant effect on the ability to regulate blood sugar, blood lipids, and eliminate foreign harmful substances. When the modified conditions are at 600 MPa, 15 minutes, and 60 °C, it is helpful to adjust the ability of blood glucose and blood lipid; The modified conditions can remove external harmful substances at 100 MPa, 10 min, and 42 °C. And this method should also be used to study the modification of cereals such as bean dregs [109]. After the soybean in the grain is subjected to high pressure treatment, it can prevent the migration of water in the soybean, make the moisture distribution in the soybean uniform, and shorten the soaking time for the production of soybean products. Scanning electron microscopy analysis showed that the microstructure of soybeans could be changed after high pressure treatment, and it could help soybeans absorb water. Found by DSC and SD-PAGE, some proteins of soybean were denatured during high pressure treatment [110].

Most of the above researchers were enriched in the studied of cereal starch, which has a modification effect on starch slurry, and can destroy the surface and internal structure particles of starch. The high pressure on the dough can increase the hardness and reduce the presence of microorganisms. The treatment of buckwheat can increase the antioxidant activity. High pressure treated grain pressure is controlled at 400–600 MPa for 10–15 min. Treated starch by high pressure can be used to make hypoglycemic food, high pressure treatment can destroy the structure of the product, loosen the surface of the raw material, and form a porous structure, thereby shortening the pretreatment time. However, for high pressure processing of cereals, there is no specific research areas have been provided. And it currently enriches in basic research. Therefore, the grain after high pressure treatment needs further excavation in food, which provides more new ideas for applied research.

3.2. Ultrafine grinding

Ultrafine grinding is a mechanical or hydrodynamic method that overcomes the internal cohesive force of the solid to break it, thereby pulverizing the material particles of 3 mm or more to 10–25 μm. In the process of ultrafine pulverization, the bean dregs are modified by friction, extrusion, collision and other forces [111]. Based on the principle of micron technology, ultrafine grinding can make the product fine in size, larger in specific surface area and specific surface activity; the ultrafine grinding product has excellent physical and chemical properties, and the utilization rate is improved [112]. Ultrafine grinding can significantly change the structure, and specific surface area of raw materials. it compared with traditional mechanical processed methods, ultrafine powders can improve the physicochemical properties of raw materials, for example, it has better hydration properties and fluidity, stronger free radical scavenging activity, flavor and mouthfeel. This new technology of superfine grinding has been proven, and used to prepare ultrafine powders with good properties [1]. At present, most countries use ultrafine grinding technology to treat pollen, tea, wheat bran, rice bran, peel, rice, soybean, beet pulp, animal bone, seaweed, edible fungi and other raw materials to preserve nutrients and improve taste [113]. At the same time, this technology has contributed greatly to the development of baked goods and other products

Used the three different grain sizes of ordinary bean dregs, hig-grade ultr-micro bean dregs powder and lo-grade ultr-micro bean dregs powder and prepare mooncakes with flour, the sensory evaluation, color and texture were used as the evaluation criteria, the results showed that the ultrafine powdered bean dregs were better than the moon cake made of ordinary bean dregs powder and formed well, the texture showed a trend of rise and then decreased. When the bean dregs powder was added to 20%, it reached the maximum value 13561.81g, as the amount of additional increased, the finished product darkens and was not easily formed. When the hig-speed ultrafine grinding bean dregs was added at 16%, the finished moon cake was the best, but if it was necessary to further increased the replacement amount of ultr-micr-bean residue. It can be considered from the point of view of bean dregs dislocation and edible rubber assisted molding. Thus preparing a wide moon cake of high dietary fiber [114]. Ultrafine grinding technology processes wheat flour and corn flour for bread production. At 9,000, 10,000, and 11,000 rpm, as the speed increases, the water retention capacity, swelling, water solubility, and gelatinization of cereal flour are improved. The quality of the product is enhanced, the volume of bread produced is increased, and the hardness is reduced [115]. The finer wheat bran granules help develop cereal bread with nutritional value. Studies have found that the amount of bi-contactable phenolic acids in whole wheat bread and brown bread is higher than white bread, and the finer bran particles in bran bread, the higher the bioacceptability of phenolic acid [116]. Both the mixing characteristics of the dough and the quality of the bread product are affected by the thickness of the bran. When the bran particle size is small, the brain cells cause rupture, which reduces the quality of the bread [117]. Micronisation has the potential to increase antioxidant activity and soluble fiber of proso bran. it can be used for enrichment of glute-free bread with fiber and phenolics [118]. The use of ultrafine grinding technology in the production of more baked goods in the grain, it can increase the aging rate of the product, and reduce the hardness of the product, it's suitable for special populations.

The application range of ultrafine pulverization was relatively wide. The use of ultrafine pulverization in tea leaves enables the tea to dissolve into the water more quickly, and the scent was more prominent and effective to save the immersion time. For example, instant tea sold on the markets. The use of ultrafine grind of Chinese medicinal materials not only enables greater medicinal properties, but also reduces the loss of scraps

and facilitates taking them. It can also introduce traditional Chinese medicine into everyday diets and develop a variety of health care products. This technology can be used on micron and submicron scales, and used in cereals such as whole wheat flour modification and related technologies [119].

Crushing whole grains with ultrafine grinding technology can improve the water absorption and stability of the flour. The exact volume area of the steamed bread was increased, and the steamed bread color was improved. The bran is ground and recombined with red wheat, and the steamed bread has a high sensory score. Therefore, ultrafine pulverization can improve the characteristics of power and improve the quality of products [120]. After the whole grain flour and starch are subjected to ultrafine grinding, reduction in starch crystallinity was resulted. Along with these structural changes, decreased viscosities and higher pasting stability [121]. Ultrafine grinding technology for preparing wheat bran dietary fiber. The results show that ultrafine pulverization can effectively pulverize fiber particles to the submicron level. As the particle size decreases, the hydration characteristics of wheat bran dietary fiber are significantly reduced, insoluble dietary fiber is converted to soluble dietary fiber, the antioxidant activity is improved, but the DPPH free radical scavenging activity is reduced [122]. Wheat bran has three kinds of ultr-fine crushing treatments with different particle sizes, and is applied to the production of steamed bread. Among them, the bran with the smallest particle diameter causes the strength of the dough to decrease, and the CO_2 produced is reduced. The exact volume area of the steamed bread becomes smaller and the hardness increases, which adversely affects the quality of the steamed bread. It can be seen that ultrafine grinding particles help improve the quality of steamed bread in a certain range, but it is not as fine as possible [123]. Ultrafine powder treats bean dregs and applies to noodles. The study concluded that compared with ordinary bean dregs, the bean dregs had a smaller particle size and increased soluble dietary fiber content. Adding bean dregs can make the dough form a stable structure, and the noodles are hard to break. Adding 7.5% ultrafine bean dregs powder reduces the cooking loss rate, almost no bean smell, and a high sensory score. Therefore, the ultrafine grinding bean dregs can significantly increase the nutritional value of the product when coupled with the noodles [124].

The above research scholars have shown that ultrafine grinding can reduce the particle size of raw materials, and improved the solubility and antioxidant activity. Superfine grinding has a wide range of applications, such as chocolate, which can increase the taste, smooth effect, and used in shells, it is a great source of calcium. Applied in the production of healthy food, if the particles are slightly larger, it will affect the taste and will not function as a health care. This requires ultrafine grinding technology, which is pulverized to a sufficiently fine particle size, and an effective mixed operation is provided to ensure uniform distribution of the food, and to facilitate absorption by the human body. Therefore, ultrafine grinding has become one of the important technologies for modern food processed, especially for health food processing. The used of this technology is currently seen in Chinese research scholars. So this technology should be respected.

3.3. Microwave

Microwave heating is now attracted much attention as an alternative heating source. Microwaves enable rapid and uniform heating of polar substances by direct and internal heating generated by friction of dipole rotations [125]. Microwave baking are easy and fast. However, for products that need to be baked for a long time, the microwave technology cannot be faced with the traditional technology. The main factor is the protein and starch in

the flour, so the formula has to be adjusted and the lo-gluten flour with protein content of 8.7% needs to be selected. The bread baked by microwave is softer and has a better shell and texture [126]. When making the bread without gluten, the addition of whey protein concentrate increases the volume and moisture content of the bread. After microwave baking, the hardness of the bread increases, the glycemic index decreases and the shelf life is prolonged, which is good for people who suffer from obesity, diabetes and celiac disease [127]. The presence of endogenous -glucanases in rice flour, can cause a substantial reduction in -glucan molecular weight, affecting detrimentally their efficacy for bioactivity. Hea-treated with microwave power (900 W) applied in cycles of 20s intervals combined with downtimes of 1 min, it was applied to the rice flours before breadmaking at flour water contents (25%) and treatment time (4 min) to reduce -glucanase activity. Bread volume is better than untreated. Microwaving rice flour helps improve glute-free bread, as well as of any -gluca-containing yeas-leavened bakery product without altering its sensorial attributes [128].

3.4 Other physical techniques

Twi-screw extrusion process to produce bean dreg-maize snack foods, it showed that the products extruded at the optimized condition had the best appearance, taste, texture and overall acceptability [129]. Electrohydrodynamic (EHD) technique improves the drying speed of bean dregs. The bean dregs cake after drying kept a whole shape and there was no cranny in the surface, the color of the sample became distinctly browner than that of the untreated [130]. Ultrasonic parameters had predictive capacity for breadmaking performance for a wide range of dough formulations Lower frequency attenuation coefficients correlated well with conventional quality indices of both the dough and the bread [131]. Bran hydration, autoclaving and freezing treatments and their combinations are promising approaches to reduce the dehydration of whole grain wheat flour dough and to improve wholegrain wheat flour bread loaf volume [132]. There is no doubt that these technology has made a great contribution to food and agricultural b-products, provides important help for the production of baked goods.

4. Improve quality of bean dregs by physical technology

4.1. Improve soluble dietary fiber of bean dregs

Soluble dietary fiber of bean dregs is a carbohydrat-based polymer with significant health benefits that is enriched in whole grains, nuts, fruits, and vegetables. In recent years, in order to increase the soluble dietary fiber fraction of fibe-rich plant food bean dregs, different approaches were investigated. At present, there are research reports on the quality improvement of bean dregs, the commonly used treatment techniques are chemical [133]. The chemical process is complex and the degree of hydrolysis is difficult. Biological [134, 135], the biological process is complex, the period is long and the condition is difficult to control. Physical approach is safer than the other two approaches, the biggest advantages come from short processing time, simple process, no solvent residue and low cost. In addition, there are many ways to combine technologies [136]. However, the combined technology has not been applied to bean dregs. Research shows that ionic liquid method, different ionic liquid treatments can significantly increase the content of soluble dietary fiber (SDF) in the bean dregs, wherein 1–ethy-3–methylimidazolium acetate > ionic liquid of

acetate > chloride ion ionic liquid, bean dreg crystal structure damaged, water holding capacity and oil holding capacity were significantly increased [137]. Soluble dietary fiber is extracted by an enzymatic method, so as to optimize the optimal process conditions of enzymatic method. Studies have found that when enzyme activity is weak. The effect of the extracted soluble dietary fiber is better than the enzyme with higher activity. However, the temperature is sometimes difficult to grasp, and if the temperature is too high, denaturation is likely to occur, which affects the reaction rated [138].

Physical processing of bean dregs is commonly used. It refers to change the chemical composition and physical structure of bean dregs dietary fiber through physical and mechanical effects such as high temperature, high pressure and high shear force, thereby improving the physical and chemical characteristics and functional quality of bean dregs. Common physical methods, such as Blast Extrusion Processing (BEP), are a new type of food processing technology. Numerous researchers have used it to improve the functional properties of cereals such as oats, glute-free flour cereals [30, 139]. This study investigated the effect of blasting extrusion processing (BEP) on the increase in soybean residue SDF content under optimal conditions (170 ℃ and an extrusion screw speed of 150 r/min). Compared with the control, the content of soluble dietary fiber from soybean residues treated by BEP (BEPSDF) was increased from 2.6±0.3% to 30.1±0.6%. In addition, BEP SDF showed improved water solubility, water retention capacity and swelling capacity [26]. Twi-screw extrusion was applied for soluble dietary fiber extraction from soybean residue. The soluble dietary fiber content of bean dregs reached 12.65%, which was 10.60% higher than that of unextruded and boiled bean dregs [140]. A novel i-situ enhanced extrusion with the aim to improve the solubility of dietary fiber in bean dregs was developed. The SDF fraction of the extrude (21.35 g/100 g) was higher than that of untreated OKP (2.30 g/100 g). The novel extrusion improved the water and oil holding as well as swelling capacities of OKP when compared to untreated and reference extrudes [141]. In addition, steam blasting technology is widely used. It puts fibrous raw materials in high pressure steam for a certain period of time. When high pressure is released instantly, the superheated steam in the raw material gap quickly vaporizes and the volume expands rapidly [142]. Use steam is blasting to treats bean dregs to make tough cookies. The results demonstrate that steam explosion has a greater impact on the composition and content of dietary fiber in bean dregs. At 1.5 MPa/30 s, the maximum soluble dietary fiber reached 36.28%. After steam blasting, the amount of bean dregs added is 10%, and the quality of biscuits is significantly improved. Therefore, the appropriate strength of steam explosion treatment can greatly improve the soluble dietary fiber in bean dregs and improve the quality of bean dregs in tough cookies [143].

Extrusion technology is used to process bean dregs to prepare soluble dietary fiber. When the liqui-solid ratio is 26: 1, at 89℃, for 68min, and alkali concentration is 1.12%. The soluble dietary fiber in extruded bean dregs were 34.12%, which was significantly higher than that of untreated (13.51%) [144]. Under the condition of microwave treatment at 200℃ for 7min, the dissolution rate of soluble polysaccharide from bean dregs increased by 70%. There is also wet grinding, bean dregs insoluble dietary fiber (IDF) was downsized to nanometer range by wet milling, which is applied as functional ingredient in foods [145]. Under the condition of microwave treatment at microwave treatment, the dissolution rate of soluble polysaccharide increased 70% from bean dregs [146]. Enzymatically prepared bean dregs dietary fiber is processed by IHP, and treated at 40, 90 and 120 MPa, respectively. The water holding capacity, expansion ratio and combined hydraulic strength was increased. The viscosity of the prepared dietary fiber solution was measured the pressure increases and rises in used rheometer. Microscopic observation of light transmittance, loose tissue, finer

fibers, improved the quality of the bean dregs dietary fiber, and there was no deterioration during refrigeration for one month. IHP can improve the quality of the bean dregs fiber, but the cost of enzymatic preparation is higher [147]. The lo-yield nuclear magnetic technology was used to study the moisture distribution of bean dregs under high pressure. Under high pressure conditions at 400MPa for 15min, the bean dregs were processed. The binding degree of bound water, flowing water and free water in bean dregs all changed significantly. High pressure treatment reduces the moisture content of bean dregs. After the high pressure treatment, most of the internal structure of the bean dregs was destroyed, wrinkles appeared on the surface, the structure shrank, and many holes were on the surface. It can reduce energy consumption for the processing of bean dregs food [148].

In recent years, great progress has been made in the research of high pressure and ultrafine grinding technology it has become a research focus in the field of enhancing the quality of bean dregs. Ultrafine grinding can effectively pulverize fiber particles to the submicron level. Insoluble dietary fiber was converted to soluble dietary fiber, and the antioxidant activity was improved [149]. Ultrafine grinding sets of different pulverization frequencies and time to process the bean dregs. Based on the physical and chemical characteristics of bean dregs, the crushing optimal parameters were obtained at a frequency of 80 Hz, and once processed. The water solubility, swelling, viscosity, and cation exchange capacity of bean dregs is significantly improved. The water and oil holding capacity of bean dregs has decreased to some extent [150]. High pressure has a significant impact on the soluble dietary fiber and functional properties of bean dregs. At 400 MPa and 60 ℃ under high pressure, the content of soluble dietary fiber increased 8 times when treated with bean dregs, compared with untreated. Swell ability and water holding (oil) properties are improved [29]. After high hydrostatic pressure treatment at 600 MPa for 30 min, the solubility of bean dregs dietary fiber is improved, which makes it more suitable for functional food processing [151]. High pressure homogenization strength is related to the solubility of bean dregs. Under high strength pressure, the structure of bean dregs particles are destroyed, and the fiber and protein of bean dregs are released [152]. Using lactic acid bacteria fermentation method and dynamic high pressure to treat bean dregs, the content of soluble dietary fiber in bean dregs was correspondingly increased, being (9.7, 14) g/100g. Insoluble dietary fiber content decreased from 11.6g/100g to (7.8, 4.5) g/100g, respectively. It can be observed that soluble dietary fiber and insoluble dietary fiber can be converted into each other under different processing conditions. There were no significant differences in dietary fiber content when bean dregs were treated under dynamic high pressure. Microstructure discovery dynamic high pressure can break down the cellulose structure and make the surface rough. The lactic acid bacteria fermentation method results in modification of the fiber structure and reduction of crystallinity [153].

It can be observed that these physical methods have significantly increased the content of soluble dietary fiber in bean dregs. The biggest advantages come from short processing time, simple process, no solvent residue, and low cost. It is possible to damage the structure of the soybean b-products during physical processing. For example, extrusion technology changes the structure of fiber molecules through intense pressure, friction and shear force, thus exposing the molecules to more soluble groups, thus increasing the content of soluble dietary fiber. Microwave has a strong penetration ability, the electromagnetic wave act on the material, resulting in the increase of the material cell pressure and expansion and rupture, the soluble dietary fiber content of bean dregs is increased. However, excessive treatment affects the content of soluble dietary fiber should pay attention to the control of treatment conditions. Typically, a combined method may have greater effects than any single approach. However, the combination of multiple technologies is rarely applied to bean dregs, especially

the combination of multiple physical technologies. Although different processing techniques improved the quality of the bean dregs to a certain extent and increased the content of soluble dietary fiber in the bean dregs. However, the ant-nutritional factors in bean dregs are the key factors affecting the quality of the bean dregs. An interesting finding is that some physical techniques can eliminate trypsin inhibitors under certain conditions.

4.2. Removal of Removal of ant-nutritional factors

Ant-nutritional factors (ANF) are substances that adversely affect the digestion, absorption, and utilization of nutrients, as well as adverse reactions that cause humans and animals. Soy was full of nutrients, but there are also a variety of ant-nutritional factors affecting the use. Ant-nutritional factor in soybean is a limiting factor, which not only hinders the body's absorption of nutrients, but also limits the comprehensive development and utilization of beans. Therefore, effectively controlling or eliminating ant-nutritional factors is one of the important ways to increase the utilization of soybeans [154]. Few types of ant-nutritional factors found in legumes that usually inhibit the bioavailability of many nutrients, such as hydrocyanic acid, trypsin inhibitors activity, phytic acids, hemagglutinins etc. However, the bean dregs contain three ant-nutritional factors: trypsin inhibitor, lectin and goitrogen, the most important is the trypsin inhibitor. These ant-nutritional factors limit the nutritional properties and affect the digestibility of certain nutrients [155]. When the researchers used bean dregs to make cookies, ant-nutritional components rise by the bean dregs ratio increase in cookies composition. The removal or degrade of the ant-nutritional factors in the bean dregs is of profound significance for improving functional food of bean dregs. Hence, further research has to initiate to decrease the ant-nutritional factors in bean dregs [156]. However, trypsin inhibitor, soybean lectin, glycinin and -conglycinin are the most important ant-nutritional factors in soybean. The bean dregs mainly contain three ant-nutritional factors: trypsin inhibitor, goitrogen and prothrombin.

4.2.1. Trypsin inhibitor. Trypsin inhibitor is a protein and about 7–10 species are found in soybeans. Among them, Kunitz trypsin inhibitor and Bowma-Bir trypsin inhibitor are the two most representative and important inhibitors. Soybean trypsin inhibitory factor (STI) is one of the main ant-nutritional factors in soybean. The content is about 2%. The ant-nutritional effects of trypsin inhibitors are mainly as follows: reducing protein digestion, inhibiting animal growth, and causing pancreatic enlargement [157]. The removal of ant-nutritional factors is mainly through physical, chemical and biological methods. In recent years, many scholars have focused on researching new and efficient methods of inactivation, such as chemical methods and high temperature transient methods, gene breeding methods, it has been able to reduce the content of trypsin inhibitors in soybeans and has been extensively studied.

After fermentation of Bacillus natto, the nutritional composition of bean dregs changed. The wet bean dregs were adjusted to moisture, sterilized, and then cooled to different concentrations of Bacillus natto, the fermentation was carried out at 37 °C for 22 h and then cooked at 4 °C for 22 h, the taste was obviously improved. Trypsin inhibitor activity and phytic acid content was significantly decreased ($P<0.05$) [158]. With bean dregs as the main raw material, used single screw extrudes in the content of bean dregs (0%, 15%, 30%, 45%), material moisture (40%), extrusion temperature (two zones: 140℃~150℃, three Area: 170℃~180℃) extrusion preparation of tissue protein. The results showed that the content of phytic acid and soluble dietary fiber increased, the activity of total phenol, total flavonoids and trypsin inhibitor decreased, the in vitro digestibility increased, and the correlation

coefficient between various nutrient factors decreased after extrusion [159]. The trypsin factor in soybean milk was treated at a high temperature of 93 C for 60–70min, and the inactivation rates reached 90%. It takes 5–10 min at 121 C, but excessive temperature and time make maillard reaction between basic amino acids such as lysine and reducing sugar, reduce the content of free amino acids, protein digestibility and nutritional value of protein [160]. In addition to, high pressure treatment can inactivate trypsin inhibitor and lipoxygenase in soybean or soy milk, and a higher pressure at 800 MPa was required for the treatment of lipoxygenase, or the combined temperature is 60 ℃ at 600 MPa. During the germination process of broad beans, use of 0.171M saline can reduce the activity of trypsin inhibitors [161].

Heat process is widely used for food preparation, which is one of an effective method used to inactive heat liable ant-nutritional factors. The heating was efficient trypsin inhibitors and lectin inactivation, being 15 min at 121 ℃ sufficient to reduce more than 90% of these compounds [162]. The trypsin inhibitor was completely inactivated after soaking soybeans in 24.3% humidity for 1 hour, and after being treated with microwave frequency at 2450 MHZ for 4 minutes, which was shorter than the heating period (6 min) needed for unsoaked soybeans [163]. Microwave treatment is an effective way for inactivation of protease inhibitor activity in cracked soybeans, roasting for only two minutes reduced the trypsin inhibitor activity to 13.33% of the initial [164]. The microwave cooking reduced ant-nutritional factors in bean thus improved the protein digestibility, while the cooking method is not studied extensively yet [165]. Roasting treatment, the processing under 230 ℃ for 25 min presented more decrease in trypsin inhibitor from soybeans [166]. Autoclaving cause significant reduce in trypsin inhibitor of chickpea [167]. Extrusion process was the best method to abolish trypsin inhibitors (99.54%), phytic acid (99.30%) and tannin (98.83%) [168]. Ultrasound treatment at 20 kHz about 20 min inactivates trypsin inhibitor by 55% [169]. High pressure processing (HPP) is another emerging novel processing technique followed in the food industry and evaluated as an alternative for the inactivation of Trypsin inhibitors. The researchers suggest that temperatures at 77–90 ℃ and pressures at 750–525 MPa less than 2 min, about 90% trypsin inhibitors inactivation [170]. At 600 MPa for 60 min at 60 ℃, 100% inactivation of trypsin inhibitors [171].

4.2.2. Lectin. The physiological activity of lectin has two side. Most lectins are resistant to digestion in human proteases, and even have adverse effects, such as stimulating the intestinal wall and impeding the digestion and absorption of nutrients. Therefore, lectins were deemed to be ant-nutrient substance. How to eliminate ant-nutrition is a matter of concern in the food processed field. Thrombin is a common ant-nutritional factor in bean dregs. It can hinder the absorption of animals.

In soybean, lectin is attended by a concentration of 10–20g/kg, which can stimulate the intestine Wall, hinder digestion, absorb nutrients and affect the metabolism of small intestinal mucosal cells, and affect the bacterial ecology in the intestine [172]. It is a glycogen protein. Defat soybean meal contains about 3% of prothrombin and is under a molecular weight of 120,000. It comprises of 4 identical subunits, each with a molecular weight of 30,000, each molecule [173]. The presence of toxic phytic acid, hemagglutinin, trypsin inhibitors and hydrocyanic acid in beans, it affects the use of food in the human body [155].

Ant-nutritional factors in velvet beans processed by ultraviolet radiation. Studies have shown that UV treated seed has lower levels of phytic acid, hydrogen cyanide and total oxalate compared to seeds soaked overnight. Ultraviolet radiation (60–90 min) completely eliminated the trypsin inhibitor activity in the seed. Both treatments completely eliminated plant hemagglutination activity [174]. Soybean hemagglutinin is not hea-resistant, and can

be inactivated quickly under hot and humid conditions. Even the activity completely disappears. Studies have shown that when purified prothrombin was dissolved in 25% sodium citrate solution. It can inhibit thrombin formation [175]. In the conventional processing, the heating method was generally adopted to remove the ant-nutrition of the lectin in the legume food, and the physiological activity of the lectin was also completely lost.

4.2.3 Goitrogen. The thyroid hormone is extremely small in soybean, and its precursor substance is glucosinolate, which was enzymatically hydrolyzed by glucosinase, and the resulting ligand further generates cyanogen, thiocyanate and isosulfur, Wherein the isothiocyanate is automatically cyclized to an oxazolidinethione under neutral conditions, and the latter three substances mainly affect the morphology and function of thyroid gland, which is the main substance leading to goiter. The pathogenic mechanism of goitre is that it preferentially binds to iodine in the blood, resulting in an insufficient source of iodine for thyroxine synthesis, leading to compensatory hyperplasia of the thyroid gland.

Soy can inactivate glucosinolates by dry heat to prevent it prevent it from producing goiter. At (90 °C, 15 min) or (100 °C, 10 min) or (110 °C, 5 min), the residual rate of enzymatically degradable glucosinolates was above 98%, but in the case of tissue breakage and the presence of aqueous media (such as germination, wet heat treatment, etc.), it was recommended that the first step of dry heat kills glucosinolates [176]. Dry heat treatment has an obvious effect on the removal of soybean goiter, and warm heat treatment has obvious effects on prothrombin and protease inhibitor. Soybean germination combined with heating treatment can remove somatostatin and protease inhibitors. Used 90 °C dry heat treatments, 15min or more, and then used 125 °C wet heat treatments for more than 10min, the ant-nutritional factor removal rate reaches 95% [177]. Dry heat treatment has a significant effect on the removal of thyroxine from soybeans, while wet heat treatment has a beneficial effect on soybean prothrombin and protease inhibitors. Dry heat treatment at 90 °C for more than 15 minutes, then the best heat treatment at 125 °C for 10 minutes, the removal rate was as high as 95%, it's convenient and energ-saving [178]. The dry heat treatment conditions were 90℃ for 15min, 100℃ for 10min, 110℃ for 5min. Inactivate glucosinolase in soybean so that it cannot enzymatic digest glucosinolates. Therefore, no goiter is produced and the residual glucosinolates can reach 98% [179].

The above researchers, whether using chemical or physical methods, can effectively remove ant-nutritional factors in beans. However, the chemical method is under a large residual amount and low safety. The sensible method commonly used is heating treatment, such as dry heat treatment or wet heat treatment, which can eliminate different ant-nutritional factors. This method is low in cost, good in effect, simply in the process, and widely used, but it takes a lot of time. The trypsin inhibitor can be inactivated under the effect of atmospheric pressure steam. If the temperature is lower than 100 ℃ for 30min, the trypsin inhibitor activity in soybean can be reduced by about 90%. In the case of hig-pressure treatment, the heating time depends on temperature, pressure, and material properties. At present, pressure baking is often used in the industry. When the temperature is between 130 °C and 133 °C, 2500kPa, soy lectin and trypsin inhibitor can be inactivated, but the disadvantage is that the cost is high and the color of the product cannot be effectively controlled. The soaking method can remove ant-nutritional factors, but it takes time and is not suitable for larg-scale production processes. The extrusion puffing method inactivates the ant-nutritional factors of soybeans, ruptures the cell wall of the raw material, and increases the digestibility of nutrients, but damages the raw material itself. Microwave treatment can penetrate into the inside of the untreated material, causing the inactivation of ant-nutritional

factors. Mechanical processing includes crushing, dehulling, etc. Many ant-nutritional factors mainly exist in the epidermal layer of crop seed. Separation through mechanical processing can reduce ant-nutritional factors. But this method is only suitable for the treatment of seed.

Conclusions

Bean dregs has high nutritional value, but it has a rough taste and has low soluble dietary fiber. Therefore, in the production of bean dregs products, special consideration should be paid to the nutrition, taste and appearance of the products, especially in baked goods. In addition, some ant-nutritional factors in bean dregs, it affects human health. At present, the most commonly used removal methods are dry heat treatment and wet heat treatment, so it is necessary to explore new processing methods, eliminate the ant-nutritional factors in the bean dregs, improve the quality of the bean dregs, and increase the added value of the products.

Relevant research shows that high pressure technology can effectively reduce microorganisms in products and extend the shelf life. The new technology of ultrafine grinding has been proven to improve the roughness of the cereals, make the power fine and improve the flavor of the product. Microwave technology is convenient and fast, which has replaced the traditional heating method. However, this method is not fully adapted to the traditional process formula, so more research is needed in the development of the product.

The combination of various technologies has become a new hot spot in recent years, which is more effective than a single technology. High pressure, ultrafine grinding and other physical technology have enormous advantages. At present, there is no research report by domestic and foreign scholars. Therefore, the combination of these two technologies is called upon to become a new type of processing technology. It can contribute to the development of high dietary fiber functional biscuits and promote the progress of baked goods. For this aspect of research, we still need a lot of research work.

Conflict of interest statement. The authors report no conflict of interest.

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Technological and chemical aspects of storage and complex processing of industrial hemp seeds

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Abstract

Introduction. The work's aim is theoretical and experimental studies of the aspects of industrial hemp seeds' storage technology, as well as the composition and quality of their processed products.

Materials and methods. Research materials are the seeds of industrial hemp of the Hliana variety, press oil, and hemp kernel. To study industrial hemp seeds' composition and quality during long-term storage (12 months), we prepared 12 polypropylene containers filled with the original hemp seeds after their initial processing.

Results and discussion. It was found that the moisture content in the seeds was 8.2–10.0%; seed purity was 97.5–99.8%; oil content was 31.9–34.3%; the weight of 1000 seeds was 17.7–19.2 g; bulk density of sources was 503,8–530 g/l. The reduction of the seeds' oil content in the second half of the shelf life was found. The yield of pressurized filtered oil increased at the end of the shelf life. The increase of the oil acid value during the seeds' entire shelf life (0.91–1.46 mg KOH/g) was detected. The peroxide value in the first half of the shelf life of hemp seeds did not exceed 5 ½ O mmol/kg, and in the second half, it increased to 10 ½ O mmol/kg. The primary unsaturated fatty acids in the studied hemp oil are oleic (14.9–19.4%), linoleic (53.4–56.6%), α-linolenic (11.3–16.2%). The ratio of essential acids ω-6 and ω-3 in the studied oil samples is close to ideal – 3.4:1–5.0:1. The yield of press cake was 67.1–70.0% at the humidity of 6.6–9.0% and at the oil content of 9.5–12.3%. The filter sludge result was 4.6–8.6% at 4.4–16.8% moisture and 49.2–64.4% oil content. The hemp kernel yield was 33.2–41.4%; content in hemp kernel: moisture – 6.9–7.8%, impurities – 0.01–0.04%. It was established that the oil content in the hemp kernel obtained from the seeds of the Ukrainian selection of the Hliana variety increased by 5.9–8.5% in comparison with the control.

Conclusions. The expediency of using the industrial hemp seeds of the Hliana variety for analytical processing at standardization of storage conditions within a year is proved.

Introduction

In current conditions, the industrial interest in hemp seeds is increasing, thanks to the knowledge of their high nutritional value and potential functionality. However, there is still a lack of awareness and a great deal of confusion between industrial and medical cannabis. There is insufficient research in the scientific literature on nutritious and healthy hemp-based foods [1].

The main parameters that affect hemp seeds' shelf life and quality are humidity, temperature, and shelf life.

There is enough information in scientific sources concerning the research of hemp seeds' storage conditions as seed material [2–5]. According to Canadian researchers, the rational conditions for long-term storage of hemp seeds (66 months) to preserve seeds' viability are a temperature of 5 °C and moisture content in the sources – 6%. The authors found no benefit from oxygen-free seed storage [2]. It should be noted that the data of work [3] on long-term storage (36 months at a humidity of 5–7%) of hemp seeds varieties cultivated in India are consistent with the data of the work [2].

According to [4], the influence of storage conditions of hemp seeds grown in Thailand on the change of their quality indicators was revealed. For long-term storage (12 months), the seeds were packed in aluminum foil and polypropylene bags. Germination and strength of seeds packaged in both types of materials at room temperature did not change for six months, and during 8–12 months of storage, germination energy decreased by 30%. The authors suggested temperature of 15 °C as the best condition for the hemp seeds' storage.

In studies [2–5], insufficient attention is paid to changes in hemp seeds' composition and quality during its long-term storage. Also, no scientific information has been found on hemp seeds' storage as raw materials for complex industrial processing.

One of the standard methods of hemp oil production is the pressing method [6]. To increase the oil yield when using the pressing technique, it is proposed to use pre-microwave treatment of hemp seeds [7], ultrasound treatment [8], and enzyme treatment [9]. In our opinion, microwave processing of oilseeds in industrial conditions is problematic in technical, energy, environmental, and social terms for humans. The use of enzyme preparations for hemp seeds' pre-treatment requires testing in an industrial setting for cost, ecology, and feasibility.

To ensure almost complete extraction of oil from hemp seeds, the method of cold pressing in conjunction with the extraction of supercritical CO_2 is used [8, 10, 11].

Studies [12] and [13] compare the yield and composition of hemp oil extracted by supercritical CO_2 extraction, n-hexane extraction using the Soxhlet method, and the press method utilizing an expeller. Extracritical CO_2 extraction revealed the highest content of tocopherols; the content of γ-tocopherol increased 2–3 times. The content of pigments (chlorophyll and carotene) in the oil also increased. The maximum oil yield (37.3%) was obtained by the Soxhlet method from hemp seeds treated with ultrasound. In [14], when liquefied dimethyl ether was used as an extractant, hemp kernel oil's yield and quality were better than when using traditional organic solvents. In our opinion, the authors' claims regarding the process' setup simplicity, economic efficiency, and the possibility of dimethyl ether recovery without traces of solvent remaining in the raw material are yet to be checked in production conditions.

The studies [15–20] research the fatty acid composition of various hemp oil samples and the ratio of essential polyunsaturated fatty acids ω-6 to ω-3. The generalized fatty acid composition depends on hemp's growing conditions [15] and the extraction of oil from seeds and its refining [16].

Seed samples used in work [17] contained 81% of polyunsaturated fatty acids: linoleic – 59.6%, γ-linolenic – 3.4%, α-linolenic – 18%. It is also noted that the oil's highest resistance to oxidation was obtained by extracting the raw material at 300 bar and 80 °C. In [15], it was found that the range of linoleic and α-linolenic acids in samples of hemp seed oil, zoned in Iran, was 57.55–63.98% and 7.57–22.91%, respectively.

In summarizing the above data, it was found that the primary unsaturated fatty acids in hemp oil samples are oleic, linoleic, α-linolenic. The ratio of essential polyunsaturated fatty acids in hemp oil is close to ideal: ω-6 and ω-3 as 2:1–3:1. From the studied sources of information, the effect of long-term storage of hemp seeds on the extracted oil's fatty acid composition was not revealed.

Work [21] presents the data on the content of micro and macroelement composition of Romanian hemp seeds in two fractions: kernels and seed coats. To improve the technology of obtaining hemp kernels and shells, the conditions and devices for implementing this process are considered. This requires further experimental production studies [31].

The aim of our work is theoretical and experimental research of industrial hemp seeds' storage technology aspects, as well as the composition and quality of the processed hemp seed products.

Materials and methods

The object of research is the technology of industrial hemp seeds' storage and processing.

Materials

Research materials are the industrial hemp seeds of Ukrainian selection of Hliana variety, press oil, and hemp seed kernel. A distinctive feature of this variety is the absence of the psychotropic substance tetrahydrocannabinol.

To ensure the biological value and competitiveness of hemp seeds and products of their processing, it is necessary to perform a systematic study of their composition and quality at different technological stages. These stages include harvesting and primary processing of hemp seeds [23], long-term storage, and complex processing. To study the composition and quality of industrial hemp seeds during long-term storage (12 months), we prepared 12 containers (polypropylene bags) filled with original hemp seeds after their initial treatment with the following indicators: mass fraction of moisture – 9.06%, seed purity – 99,75%, the mass fraction of oil, in terms of dry matter – 32.99%, acid value of fat – 0.65 mg KOH/g, peroxide value – 2.63 ½ O mmol/kg, the weight of 1000 seeds – 17.74 g [23]. The study began on October 10, 2018. The indexation of industrial hemp seeds' samples to study its composition and quality: 0 – the original model (October 2018), the following samples (1–12) were taken at intervals of one month (November 2018 – October 2019). 12 samples of oil and 12 samples of hemp kernel were obtained from each piece of stored industrial hemp seeds. The indexation of oil and hemp kernel samples corresponded to the original industrial hemp seed samples' indexation.

Samples of hemp oil were obtained using a PCI 250 screw press, and examples of hemp seed kernels were obtained using an experimental centrifugal device to isolate the kernel.

Obtaining prototypes of hemp oil by cold pressing

Preparation of samples. Hemp oil production differs from other oilseeds in that there is no "raw material preparation" stage before pressing. Before loading into the auger, hemp seeds are not subject to wet-heat treatment and don't require cleaning from the shells, but must comply with the current regulatory documentation requirements for humidity and degree of purity. Therefore, before extracting oil from industrial hemp seeds, each sample was controlled according to these parameters monthly for a year.

Description of methods and settings. A PSh-250 screw press, designed for continuous cold pressing of vegetable oils from oilseeds was used to obtain the oil. The design of the auger, the auger chamber, and the grain cylinder allow for optimal temperature and pressure conditions for pressing oilseeds and ensures the required degree of oil recovery. The productivity of the screw press PCI-250 is 150 kg/h, the yield of unfiltered oil is 22.8–24.2%, the output of cake is 50.1–66.7%, the oil temperature at the outlet of the press is up to 55 °C.

Order of research. The raw material was uniformly fed into the inlet of the screw press, and then it was fed into the grain chamber. In the working section of the press, a screw shaft acted on the raw material, due to which the squeezing and extraction of the liquid phase from the seeds — oil — took place. The grain compartment's bottom and walls have slots through which the oil flowed into the storage tank, which was located at the bottom, and the petals came out as press cake at the end of the horizontal working zone.

Oil purification was carried out by sedimentation filtration. Oil in the amount of 20 liters was loaded into bag filters with gabardine fabric, which had the following characteristics: height – 75 cm, filtration area – 0.94 m^2, filters were placed above the storage tanks. The duration of oil cleaning was 24 hours. The disadvantage of this filtration method is the direct contact of the oil with air, which increases the risk of oxidation of the finished product.

Production losses during pressing and filtration were the material's adhesion to the press's working organs, to the filter cloth, and to the inner surface of the containers into which the oil entered.

Processing of research results. The finished product yield was calculated as a percentage of the total weight of the raw material.

Obtaining prototypes of hemp kernel

Preparation of prototypes. Before isolating the kernel from industrial hemp seeds, each sample (monthly for a year) was controlled for moisture and purity.

Description of methods and settings. Separation of shells from industrial hemp seeds was performed on an advanced experimental centrifugal device (Figure 1, patents for utility model UA 122649 Device for crushing hemp seeds and UA 135810 Method collapsing industrial hemp seeds). The productivity of the device for isolating the hemp kernel is 80–100 kg/h. The working body's rotation speed is 1000–2500 min^{-1}, the drive power is 0.7 kW, and the dimensions of the device, m: body diameter – 0.38 and height – 0.34. The shape of the working body (wheel or disc) of the hemp kernel release mechanism affects the ability to break down the seed coat. The method of single-oriented impact [24], which is implemented in this device's design, is sufficient for the collapse of oilseeds. The impeller of a closed sectoral type has the prospect of further use, which requires additional production and experimental research [22].

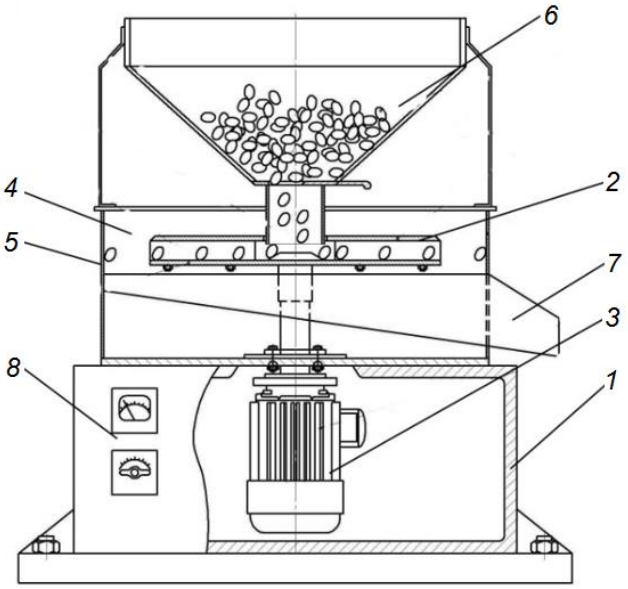

Figure 1. Device for collapsing hemp seeds:
1 – frame (frame, body, base); 2 – impeller; 3 – electric motor; 4 – working chamber; 5 – jack deck; 6 – bunker; 7 – unloading tray; 8 – control devices.

The impeller of the experimental device consists of two disks, the upper one of which has a loading opening, four sectors located between the disks and together form four radial profile channels with a hyperbolic shape of the lateral surfaces, a b

affle deck, made in the form of a cylinder with a smooth inner surface, an unloading chute has W-shaped in cross-section.

Research procedure. Industrial hemp seeds were loaded into hopper 6 of the device. Through the branch pipe and the loading hole in the upper disc, it fell on the lower disc 2. Under the action of centrifugal forces, the seeds began to move in the horizontal plane on the profile channels in the direction of the bumper deck 5. At the moment of the seed's contact with the deck, the fruit shell was destroyed, and the kernel was released. The resulting mixture fell onto the unloading chute seven and was removed from the device under the influence of vibration.

The resulting mixture was sieved successively on sieves with round and oblong holes. The separation by aerodynamic properties was carried out on a gravity air separator with an open vertical air cycle.

Processing of research results. The finished product yield was calculated as a percentage of the total weight of the raw material**.**

Determination of mass fraction of moisture

Preparation of prototypes. The initial weight of industrial hemp seeds and their processing products is 30 g. 5 g of seeds, kernels, cake, or sludge were weighed into two boxes [25, 26].

Description of methods and settings. The mass fraction of moisture in industrial hemp seeds and their processing products was measured via the thermogravimetric method in an oven with adjustable temperature [24].

Research procedure. Prepared weighing bottles with samples were placed in an oven and dried at 105 °C for 40 min (first weighing) and subsequent considering every 10 min until constant weight. After drying, the weighing bottles were removed from the cabinet with crucible tongs and placed in a desiccator for cooling for 15–20 minutes [26].

Processing of research results. Chilled weighing bottles were weighed closed on an analytical balance. Humidity was calculated to one decimal place according to the formula (1):

$$W = \frac{m_2 - m_3}{m_2 - m_1} \cdot 100\%, \quad (1)$$

where: m_1 – the weight of the empty box, g;

m_2 – importance of a box with a sample before drying, g;

m_3 – importance of a box with a model after drying, g.

Oil content measurement

The oil content in industrial hemp seeds and products of their processing was measured by the method of exhaustive extraction in a Soxhlet apparatus [27].

Measurement of acid and peroxide values. The acid and peroxide values of pressed hemp oil samples were measured by the titrimetric method according to [28].

Measurement of fatty acid composition

The fatty acid composition of pressed hemp oil samples was determined by gas-liquid chromatography according to the method described in [26, 29].

Results and discussion

Indicators of industrial hemp seeds' quality during long storage

Characteristics of the composition and quality of industrial hemp seeds of Hliana variety during the storage for 12 months are given in Table 1.

Table 1

Characteristics of physical and chemical quality indicators of industrial hemp seeds of Hliana variety

Samples	Moisture content,%	Seed purity,%	Oil content,%	Weight of 1000 grains, g	Bulk density, g/l
0	9,1±0,03	99,8±0,2	33,0±0,1	17,7±0,5	506,0±5
1	8,7±0,03	99,2±0,3	33,5±0,1	17,8±0,5	507,2±5
2	9,1±0,03	99,6±0,3	33,6±0,1	19,2±0,5	508,3±5
3	10,0±0,04	98,6±1,3	34,3±0,1	17,9±0,5	503,8±5
4	9,7±0,03	98,6±1,4	33,4±0,1	18,4±0,5	504,7±5
5	10,1±0,04	98,5±1,4	34,0±0,1	19,2±0,5	507,2±5
6	8,2±0,03	98,2±1,7	33,3±0,1	19,1±0,5	520,0±5
7	9,8±0,04	98,1±1,8	33,2±0,1	18,4±0,5	505,5±5
8	8,6±0,03	98,1±1,7	33,2±0,1	19,0±0,5	510,2±5
9	8,7±0,03	97,6±2,3	32,8±0,1	19,1±0,5	510,1±5
10	8,7±0,03	97,5±2,4	32,6±0,1	18,6±0,5	520,2±5
11	8,9±0,03	97,5±2,4	32,2±0,1	18,8±0,5	526,0±5
12	9,0±0,03	97,5±2,4	31,9±0,1	19,0±0,5	530,0±5
Control	≤11,0	≥90,0	≥30,0	-	-

Note: [a)] 0 – the original sample (October 2018), the following examples (1–12) were taken at intervals of one month (November 2018 – October 2019);
[b)] in terms of dry matter;
[c)] the quality of the control sample was limited by the current technical requirements for industrial hemp seeds.

When analyzing the data in Table 1, it was found that during the long-term storage of industrial hemp seeds:

- The fluctuations in moisture content in seeds are explained by the influence of temperature and air humidity on its hygroscopicity;
- The purity of the seeds was within 97.5–99.8%, which exceeds the value of the control sample;
- The seeds' oil content was in the range of 31.9–34.3%, which is more than the control sample's respective value. The oil content in the seeds decreases from the second half to the end of the storage period (Figure 2), which is explained by the course of biochemical processes in it during long-term storage;
- The mass of 1000 seeds was in the range from 17.7 to 19.2 g, and the bulk weight of seeds was from 503.8 to 530 g/l. For the control sample, these technical indicators are not regulated.

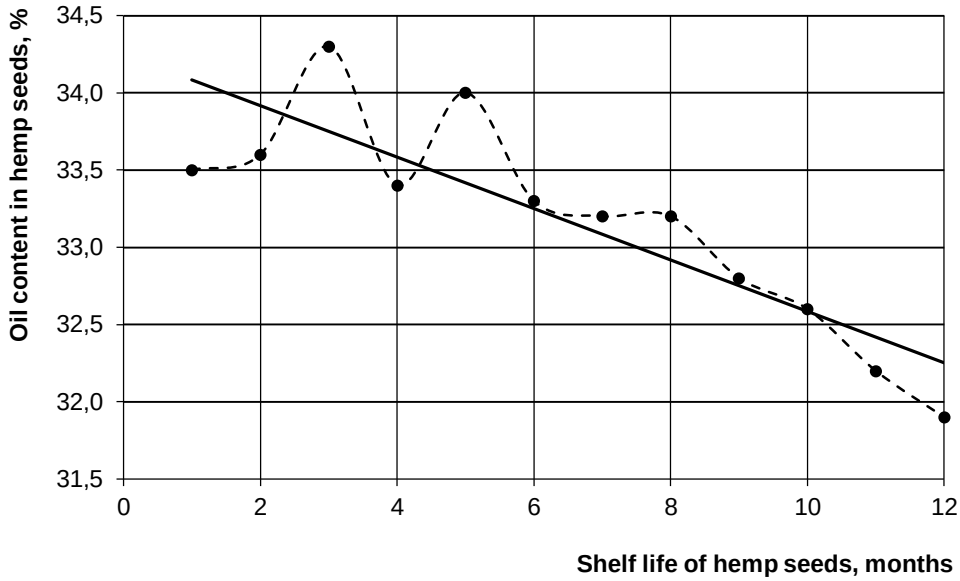

Figure 2. Dependence of oil content in industrial hemp seeds on their shelf life

The obtained data on the oil content in hemp seeds are correlated with the data of Morar M. V., Abdollahi M., Kriese U., and others [6, 15, 18]. The obtained data on the mass of 1000 seeds and a bulk pack of industrial hemp seeds of Hliana variety corresponds to the data of Klevtsov K. for sorts Zolotoniski and YUSO-31 [30].

Therefore, the above data show the possibility of using industrial hemp seeds of Hliana variety for rational processing to standardize storage conditions during the year.

Yield and quality indicators of hemp press oil

Hemp oil is a rare source of nutrition for the body due to a unique ratio of fatty acids ω-6 and ω-3 as 3:1. It is beneficial for the health of the cardiovascular system, skin, hormonal balance, diabetes prevention, and more. This feature of the oil helps to increase the industrial production of quality finished products [12].

Quality indicators of 13 samples of pressed, filtered oil obtained from industrial hemp seeds of the Ukrainian selection of Hliana variety are presented in Table 2.

Table 2

Yield characteristics and physical and chemical quality indicators of filtered pressed hemp oil

Samples	Air temperature during pressing, ℃	Oil temperature at the outlet of the press, ℃	The yield of filtered oil,%	Acid value, mg KOH/g	Peroxide value, ½ O mmol/kg
0	-	-	-	0,91±0,07	6,0±0,2
1	-	-	16,6	0,91±0,07	3,6±0,1
2	-	-	15,5	0,94±0,07	4,4±0,1
3	-1	77,4	14,6	0,95±0,07	3,5±0,1
4	0	81,4	16,8	1,01±0,07	1,1±0,08
5	4,2	79,4	16,2	1,04±0,07	2,5±0,1
6	8,3	83,5	16,6	1,09±0,07	3,6±0,1
7	16,0	86,2	17,1	1,12±0,07	8,4±0,3
8	22,1	83,0	16,8	1,25±0,07	9,9±0,3
9	19,9	88,7	19,2	1,34±0,07	9,3±0,3
10	22,0	84,2	18,4	1,39±0,07	7,9±0,3
11	20,7	85,3	19,3	1,42±0,07	5,8±0,2
12	11,5	74,5	19,1	1,46±0,07	6,0±0,1

Note: [a] 0 – oil obtained from the original sample of industrial hemp seeds (October 2018), the following examples (1–12) – oil obtained from industrial hemp seeds with an interval of one month (November 2018 – October 2019).

From the analysis of the data, Table 2 found that:

- The air temperature during pressing was in the range from -1 to +22.1℃;
- The oil temperature at the outlet of the press ranged from 74.5 to 88.7℃. The increase in oil temperature can be explained by the influence of air temperature and the equipment's design features. The search for rational modes of pressing the material to reduce the oil temperature at the outlet from the press to reduce the degree of its oxidation seems obvious;
- When packing the hemp seeds samples for long-term storage, the oil yield after filtration ranged from 14.6 to 19.3%. An increased product of filtered oil was obtained by pressing samples 9–12 (Figure 3);
- The acid value in the obtained oil samples ranged from 0.91 to 1.46 mg KOH/g (Figure 4). The obtained data do not exceed the normative amount of 1.5 mg KOH/g;
- In the first half of the shelf life of hemp seeds (samples 1–6), the oil's peroxide value did not exceed 5 ½ O mmol/kg. In the second half of the shelf life (samples 7–12), the oil's peroxide value increased to 10 ½ O mmol/kg. This is due to the increased storage temperatures of hemp seeds from May to August. It should be noted that it is advisable to conduct a study on filtered hemp oil oxidation over time to determine the totox value [25, 29].

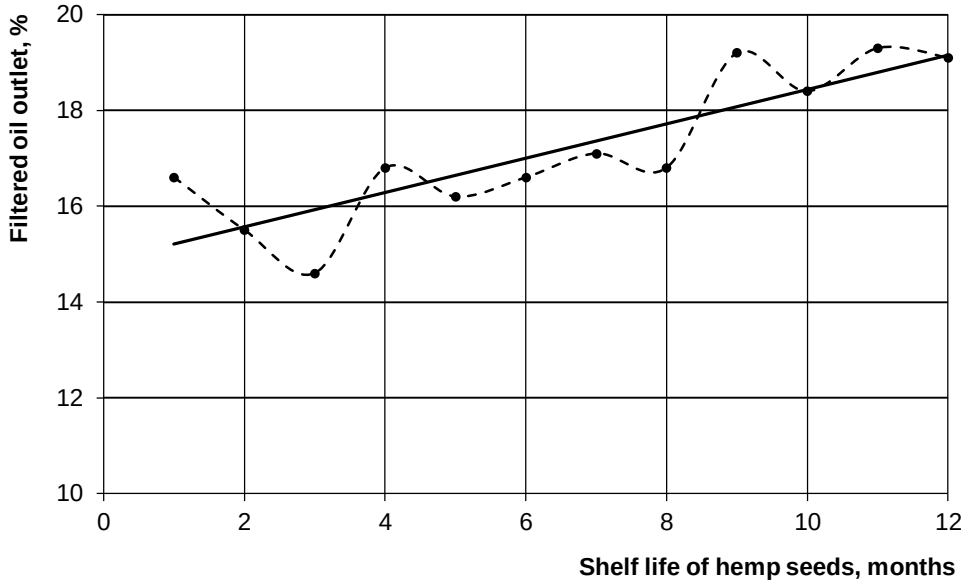

Figure 3. Dependence of the yield of filtered hemp oil on the shelf life of raw materials

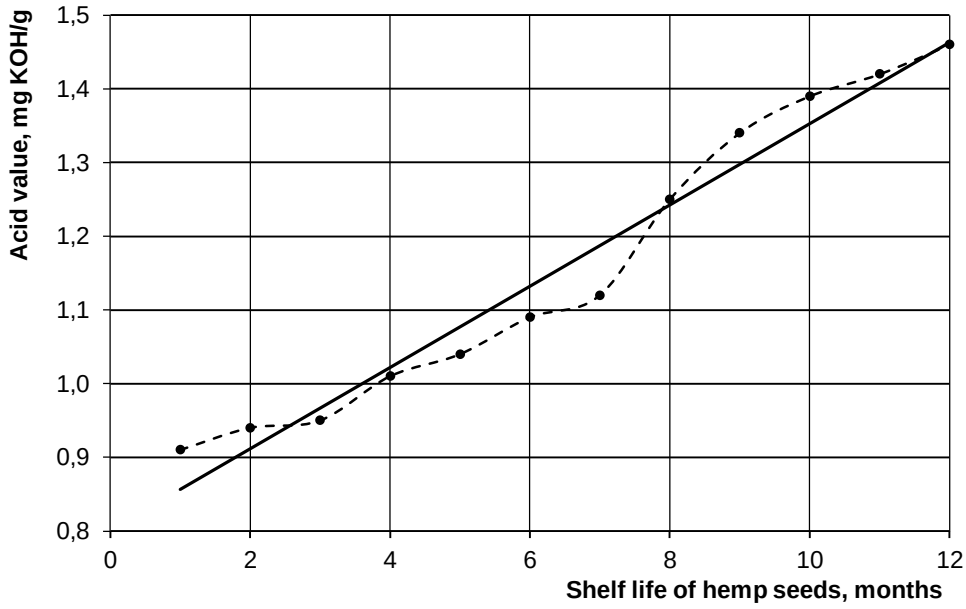

Figure 4. Dependence of the acid value of pressed hemp oil on the shelf life of raw materials

The yield of unfiltered pressed hemp oil in samples 1–12 (22.5–24.2%) is consistent with the yield of oil in the studies of C. Da Porto, K. Aladic, and others [8, 10, 17].

The oil content in our experimental samples of 1–12 seeds of industrial hemp was 31.9–34.3% and in the examples of work [6] – 30.89–33.25%. The obtained yield of pressing oil (samples 1–12) is 2% less than the product of oil in the study [6]. This is explained by the design features of the PSh-250 screw press, technological modes of pressing and indicates the need to improve the technology of pressing industrial hemp seeds.

The obtained data on the acid and peroxide values of experimental samples of press hemp oil is 1–12 less compared with the data of Morar M. V. and others [6] by 3 mg KOH/g and 17 ½ V mmol/kg. This can be explained by the difference in the technology of preparation and pressing of hemp seeds.

Analysis of the fatty acid composition of pressed hemp oil

To confirm the data on the biological value of hemp oil obtained from the seeds of the Ukrainian selection of the Hliana variety, its fatty acid composition was studied. The study results of the content of fatty acids in pressed hemp oil are given in Table 3.

When analyzing the data on the fatty acid composition of hemp seed oil in long-term storage (Table 3), it was determined that:

- the content of saturated fatty acids was: myristic – from 0.1 to 0.2%, palmitic – from 5.6 to 6.6%, stearic – from 3.3 to 3.5%, arachidonic – from 0.9 to 1.9%, behenic – from 0.2 to 0.9%, lignoceric – from 0.1 to 0.5%;
- the content of unsaturated fatty acids was: palmitoleic – 0.1%; oleic – from 14.9 to 19.4%, linoleic – from 53.4 to 56.6%, α-linolenic – from 11.3 to 16.2%, γ-linolenic – from 1.6 to 2.6%, gadoline – from 0.4 to 1.9%, gondoic – from 0.8 to 0.9%, dihomolinolenic – from 0.3 to 0.4%, erucic – from 0.1 to 0.4%, docosadienoic – from 0.5 to 0.7%, nervonic – 0.2%;
- the main unsaturated fatty acids in the studied hemp oil are oleic (14.9–19.4%), linoleic (53.4–56.6%), α-linolenic (11.3–16.2%);
- the ratio of essential polyunsaturated fatty acids in the studied samples of hemp oil is close to ideal (3:1÷5:1 [29]): ω-6 and ω-3 as 3,4:1÷5,0:1. Today, the exceptional importance of ω-3 polyunsaturated fatty acids for maintaining physical and mental health and preventing some diseases [25, 29].
- The obtained data on the fatty acid composition of experimental samples of hemp oil is correlated with the data [15–17].

Yield and quality indicators of by-products obtained in the production of filtered press hemp oil

Data on the yield and physicochemical parameters of by-products obtained in filtered pressed hemp oil production are presented in Table 4.

Table 3

Fatty acid composition of pressed hemp oil

N	Fatty acid	Fatty acid content of the sample,%												
		0	1	2	3	4	5	6	7	8	9	10	11	12
1	C 14:0 myristic	-	-	-	-	-	-	-	-	-	-	0,1	-	0,2
2	C 16:0 palmitic	5,8	5,9	5,8	5,6	5,8	5,8	5,7	5,8	5,9	6,1	6,2	6,1	6,6
3	C 16:1 palmitoleic	0,1	-	-	0,1	0,1	-	-	-	0,1	0,1	0,1	0,1	-
4	C 18:0 stearic	3,4	3,3	3,4	3,3	3,4	3,4	3,4	3,3	3,4	3,5	3,4	3,5	3,4
5	C 18:1 oleic	15,1	19,3	15,7	15,3	15,1	15,9	18,0	15,4	15,0	14,9	14,9	15,6	19,4
6	C 18:2 linoleic	54,6	55,8	54,1	54,9	54,9	54,9	53,4	55,3	54,2	54,0	54,6	54,4	56,6
7	C 18:3 α-linolenic	15,5	11,6	15,6	15,6	15,8	15,4	14,8	15,4	15,5	15,5	16,2	15,7	11,3
8	C 18:3 γ-linolenic	2,5	1,8	2,4	2,4	2,5	2,4	2,3	2,4	2,5	2,5	2,6	2,4	1,6
9	C 20:0 arachidic	1,8	-	-	-	0,9	1,5	1,6	-	1,8	1,9	-	-	-
10	C 20:1 gadoleic	0,4	0,8	1,0	0,9	0,8	0,4	0,4	0,7	0,4	0,4	1,9	1,5	0,5
11	C 20:2 gondoic	-	-	-	0,8	-	-	-	0,9	-	-	-	-	-
12	C 20:3 digomo linolenic	-	-	-	0,4	-	-	-	0,3	-	-	-	-	-
13	C 22:0 behenic	0,4	0,5	0,9	0,4	0,4	0,3	0,4	0,2	0,6	0,4	-	0,7	0,4
14	C 22:1 erucic	-	0,3	0,4	-	0,1	-	-	-	0,1	-	-	-	-
15	C 22:2 docosadienoic	-	0,5	0,7	-	-	-	-	-	-	-	-	-	-
16	C 24:0 lignoceric	0,2	0,2	-	0,1	0,2	-	-	0,1	0,3	0,5	-	-	-
17	C 24:1 nervonic	0,2	-	-	0,2	-	-	-	0,2	0,2	0,2	-	-	-

Table 4

Characteristics of the yield and physicochemical indicators of the quality of related products obtained in the production of filtered press oil from hemp seeds for long-term storage

Samples	Press cake, %	Moisture content in the cake,%	Oil content in the cake[s],%	Yield of filter sludge,%	Moisture content in the sludge,%	Oil content in the sludge,%
1	68,0	-	-	6,6	-	-
2	68,3	7,5±0,01	12,3±0,06	7,8	4,4±0,01	60,6±0,3
3	69,0	7,4±0,01	11,1±0,05	8,6	4,6±0,01	64,4±0,3
4	67,8	6,6±0,01	10,1±0,05	7,4	13,7±0,02	59,1±0,2
5	68,6	9,0±0,01	11,9±0,06	6,3	11,6±0,02	51,5±0,2
6	69,2	7,8±0,01	10,9±0,05	6,6	11,7±0,02	59,4±0,2
7	69,0	7,6±0,01	10,8±0,05	6,7	11,2±0,02	57,4±0,2
8	68,5	8,0±0,01	11,1±0,05	5,9	10,3±0,02	49,6±0,2
9	70,0	6,8±0,01	9,5±0,04	4,7	16,8±0,03	49,2±0,2
10	69,0	7,2±0,01	10,2±0,05	5,7	10,2±0,02	50,20±0,2
11	68,6	7,9±0,01	10,5±0,05	4,6	8,1±0,01	55,42±0,2
12	67,1	8,5±0,01	10,9±0,05	4,9	7,0±0,01	56,57±0,2

Note: [a)] samples (1–12) are by-products obtained from the production of industrial hemp seeds with an interval of one month (November 2018 – October 2019); [b)] in terms of dry matter.

From the analysis of data Table 4, it follows that:

- The yield of the cake was from 67.1 to 70.0% at a moisture content of 6.6 to 9.0% and an oil content of 9.5 to 12.3%;
- The yield of filter cake was from 4.6 to 8.6% at a humidity of 4.4 to 16.8% and an oil content of 49.2 to 64.4%. To reduce the oil and moisture content in the filter sludge, it is advisable to streamline the technological process of obtaining and filtering pressed hemp oil.

Yield and quality indicators of hemp kernel

Data on yield and physicochemical quality indicators of hemp kernel are presented in Table 5.

From the analysis of data Table 5, it follows that:

- the yield of hemp kernel ranged from 33.2 to 41.4%; cuttings were from 0.6 to 5.2%, substandard seeds were from 1.3 to 4.8%, intermediate products were from 53.3 to 61.2%;
- content in hemp kernel: moisture was in the range from 6.9 to 7.8%, oil was from 53.9 to 56.5% (Figure 5), impurities were from 0.01 to 0.04%. Fluctuations in the hemp kernel's moisture content are explained by the previous effect on the hygroscopicity of the stored seed temperature and humidity. It should be noted that the studied samples of hemp kernel obtained from the seeds of the Ukrainian selection of the Hliana variety contain 5.9–8.5% more oil compared to the control (48% [29]).

Table 5

Characteristics of the yield and physicochemical indicators of the quality of experimental samples of the kernel obtained from hemp seeds of long-term storage

Samples	Yield,%				Content,%		
	Hemp kernel	Chaff	Substandard seeds	Intermediate products[c]	Moisture	Oil[d]	Impurities
0	36,0	1,4	4,8	57,8	7,0±0,02	53,9±0,2	0,02±0,001
1	41,4	1,4	3,9	53,3	7,0±0,02	54,5±0,2	0,02±0,001
2	40,6	1,3	2,8	55,3	7,2±0,02	54,3±0,2	0,02±0,001
3	33,2	0,7	7,9	58,2	7,1±0,02	56,2±0,2	0,02±0,001
4	36,6	0,9	2,5	60,0	7,8±0,03	56,5±0,2	0,03±0,002
5[e]	-	-	-	-	-	-	-
6	35,3	5,2	1,3	58,2	6,9±0,02	55,0±0,2	0,02±0,001
7	39,1	0,6	2,0	58,3	7,7±0,03	55,5±0,2	0,03±0,002
8	34,8	1,4	3,2	60,6	6,9±0,02	55,1±0,2	0,04±0,002
9	34,9	1,6	3,8	59,7	6,9±0,02	55,1±0,2	0,02±0,001
10	35,2	2,7	2,6	59,5	7,0±0,02	54,5±0,2	0,02±0,001
11	36,2	1,9	3,1	58,8	7,1±0,02	54,3±0,2	0,01±0,001
12	34,4	1,5	2,9	61,2	7,3±0,03	54,1±0,2	0,03±0,002
Control[f]	-	-	-	-	≤7,0	≥48,0	-

Note: [a)] 0 – hemp kernel obtained from the original sample of industrial hemp seeds (October 2018), the following samples (1–12) – hemp kernel obtained from industrial hemp seeds with an interval of one month (November 2018 – October 2019);

[b)] sources with partially or entirely unseparated fruit skin;

[c)] a mixture of elements of industrial hemp seeds after separation of the kernel;

[d)] in terms of dry matter;

[e)] these studies are absent due to force majeure;

[f)] data of work are accepted for comparison [29].

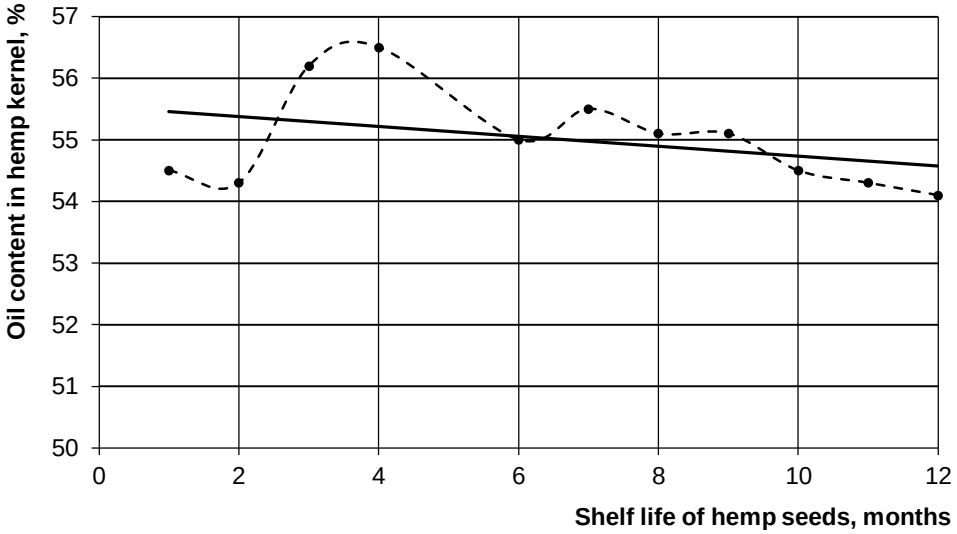

Figure 5. Change in the oil content of hemp kernels during the long-term storage of seeds

The decrease in the hemp kernel's oil content is due to the biochemical processes of life of the industrial hemp seeds and the conditions of their long-term storage.

Conclusions

1. The expediency of using the industrial hemp seeds of the Hliana variety for analytical processing at standardization of storage conditions within a year is proved.
2. To reduce the oxidation of pressurized oil, it is necessary to rationalize pressing hemp seeds. When pressing hemp seeds for long-term storage, filtered oil yield from 14.6 to 19.3% was obtained. The acid value in the obtained oil samples ranged from 0.91 to 1.46 mg KOH/g, which does not exceed the normative amount. In the first half of the shelf life of hemp seeds, the peroxide value of oil did not exceed 5 ½ O mmol/kg; in the second half, it increased to 10 ½ O mmol/kg.
3. The primary unsaturated fatty acids in the studied hemp oil are oleic (14.9–19.4%), linoleic (53.4–56.6%), α-linolenic (11.3–16.2%). The ratio of essential polyunsaturated fatty acids in the studied hemp oil is close to ideal: ω-6 and ω-3 as 3.4:1–5.0:1.
4. The yield of hemp kernel ranged from 33.2 to 41.4%. The oil content in the hemp kernel obtained from the seeds of the Ukrainian selection of the Hliana variety increased by 5.9–8.5% compared to the control (48%).

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Effect of natural sugar substitutes – mesquite (*Prosopis alba*) flour and coconut (*Cocos nucifera* L.) sugar on the quality properties of sponge cakes

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Abstract

Introduction. The aim of the research was to evaluate the physico-chemical and microbiological characteristics of sponge cakes with natural sugar substitutes – mesquite (*Prosopis alba*) flour and coconut (*Cocos nucifera* L.) sugar.

Materials and methods. The sponge cake was prepared from wheat flour, sugar, eggs with the addition of Coconut sugar and mesquite flour in ratio 3:1 as natural sugar substitutes. The sponge cakes with 100% sugar substitutes were processed at constant regime of baking concurrent with that of the control sample.

Results and discussion. Specific volume of cakes varied between 2.92±0.10 cm^3/g and 3.13±0.11 cm^3/g. In this studying the volume of the cake with sugar substitutes was smaller than this of cake control (219.00±2.07 cm^3). The greatest porosity was observed in the cake control (63.23±1.30%). The water-absorbing capacity of the cake with coconut sugar and mesquite flour (315.60±3.08%) is the lowest than that of the cakes cake control. Baking losses of all the samples were in the range of 15.27–17.55%. Sugar substituted cakes had less baking loss and was statistically different from control. Cake crust of control sample had the highest values of L* (58.46±2.25), a* (9.56±0.62) and b* (25.31±0.82). The crumb and crust color of cake with coconut sugar and mesquite flour mix was brownish and darker than cake control crumb and crust. The highest fat content was defined in the sample control (6.89%) and the lowest content was in the cake with coconut sugar and mesquite flour (5.66%). The highest percentage of carbohydrate was determined in the control (58.21%), as with the lowest content was the cake with coconut sugar and mesquite flour (23.50%). It is important to note that sponge cake with natural sugar substitutes could be tagged as foods and could support the claim "with high content of dietary fiber". The energy value of the cake with coconut sugar and mesquite flour being the lowest – 209.98 kcal/100g of product, with 37% lower than the control cake. From microbiologycal point of view results of to the first day of storage at room temperature, no evidence of pathogenic bacteria and mold was detected on the samples.

Conclusions. The sponge cake made with composite coconut sugar and mesquite flour exhibited fairly good technological characteristics. From a functional and nutritional point of view, these cakes contained significantly higher levels of dietary fiber than the traditional bakery products prepared with sugar.

Introduction

Sugar reduction or removal in confectionary products is an important research objective for the food industry, considering negative press, consumer awareness around civilisation diseases and government strategies for sugar reduction in high sugar products [1].

Some studies with different *Prosopis* species indicated that it is a good source of carbohydrates, lipids, minerals, and phytochemical compounds with beneficial effects on health [2].

Mesquite flour was previously tested in simple bread formulations. MF addition in non-sweet breads modified their sensory characteristics and technological quality (specific volume, crumb texture and porosity). However, the fiber content was significantly increased by MF addition allowing obtaining fiber enriched breads [3–4]. Taking into account the particular color and flavor conferred by mesquite flour, it was considered that these characteristics would make it a good ingredient for sweet bread/cake formulations. Sweet bakery comprises a large number of products due to the great variety of ingredients that can be used in it. Mesquite flour is the product obtained by grinding the whole pods. Besides fibre, it also has proteins, lipids and provides calcium and iron, among other minerals. The level of protein is variable (7-11 g/100g) [4–5]. It is not found the scientific evidence about application of mesquite flour as sugar substitute in the cakes and influence on quality papameters.

Leguminous flours can provide both nutritional and functional benefits when added to a bakery product formula. They are usually a good source of dietary fibre and leguminous proteins are complementary to cereal proteins. When combined in composite dough, a protein mixture with higher nutritional value is obtained [6–7]. Prokopiuk et al., 2000 [5] reported 27 g/100g of total dietary fibre in *Prosopis alba* pulp. Mesquite flour is the product obtained by grinding the whole pods. Besides fibre, it also has proteins, lipids and provides calcium and iron, among other minerals. The level of protein is variable (7-11 g/100g) [4–5]. Several authors [7–9] found that the replacement of wheat flour with different amounts of leguminous flours or protein isolates obtained from them (chickpea flour, soy flour, mesquite flour) affected the rheological properties of dough due to network weakening and consequently, the quality of the final product such as volume, internal structure and texture of the breads [10]. Bigne et al., 2016, 2018 [3–4] reported that the high level of fibre in mesquite flour led to changes in the textural properties of dough, as a consequence of an inferior development of the gluten network. Higher levels of added mesquite flour led to dough with increased consistency and less cohesiveness, where a disruption of the gluten matrix was observed. However, there are unexplored legumes that have the potential for inclusion in the food industry, such as some species of *Prosopis* pods. Until now, there are a few studies on the flour obtained from these pods, and the impact of its inclusion in the bakery. In this section will be discussed the information about the pods, the obtained flour, and the bakery products with this ingredient.

Prosopis flour (PF) is described as brown and sweet with hints of coffee, cocoa, coconut, caramel or molasses, cinnamon, and hazelnut [2]; and has approximately equal energy and proteins content comparing with wheat flour, besides it is gluten-free [11]. PF production varies according to the pod and seed characteristics. Bigne, Puppo & Ferrero, 2016 [4] mentioned that PF is obtained by grinding the whole pods. Despite the full range of food that can be prepared from PP and PF, the inclusion of PF in bakery products is of particular interest among other legumes.

Coconut (*Cocos nucifera* L.) palm is a monocotyledon belonging to *Arecaceae* or *Palmae* family. Coconut palm can be processed into coconut water, coconut milk, coconut

sugar, coconut oil, and coconut meat. Coconut has a glycemic lowering effect. Low glycemic index food particularly such containing high dietary-fiber, has been demonstrated to moderate post-prandial blood glucose and insulin responses enhancing blood-glucose and lipid concentrations in humans and patients having diabetes mellitus [12].

Coconut (*Cocos nucifera*) contains higher amounts of dietary fiber (60 g/100 g) and other nutrients [12]. Coconut contains low amount of digestible carbohydrates, and has no gluten. Nutritional composition of coconut flour is quite comparable to that of wheat flour. There is an apparent need to convert the food processing byproducts into functional ingredients in order to implement their environment-friendly and efficient utilisation.

Coconut sugar is made by heating of inflorescence sap until it turns to brown and granulate, it has been a growing interest in Europe and North America as a natural sugar alternative because it has low glycemic index around 35. Coconut sugar usually uses as an ingredient in many foods and drinks to provide a pleasant flavor. Coconut flour and sugar was successfully incorporated into bakery, extruded products and traditional sweets [13–14].

The above-presented brief review on available data clearly identifies the lack of sufficient scientific evidence about the effects of these sugar substitutes on the physico-chemical and microbiological characteristics of sponge cakes. It is not determined the scientific evidence about application of mesquite flour as sugar substitute in the cakes.

The aim of the research was to evaluate the physico-chemical and microbiological characteristics of sponge cakes with natural sugar substitutes – mesquite (*Prosopis alba*) flour and coconut (*Cocos nucifera* L.) sugar.

Materials and methods

Preparation of sponge cakes

The control cake was prepared, following a traditional technology and formulation [15]. The batter formulation of the control cake was as follows (based on batter weight): egg yolk 13.35%, egg white 29.88%, refined granulated sugar 25.90%, and wheat flour 30.88%. In particular, a double mixing procedure was applied by partitioning whipping of whites and egg yolks. Coconut sugar and mesquite flour were added in cake batter in ratio 3:1 as natural sugar substitutes.

Sugar is the main ingredient of the control cake formulation (about 26% of the batter ingredients). For the modified samples, the sugar substitutes mix from coconut sugar and mesquite flour was added to replace sugar (100% replacement). The recipe compositions of the control sample and the investigated cakes containing sugar substitutes mix are presented in Table 1.

The stages of technology were kept because of their easy fulfillment and the considerably small duration of the technological cycle. The sponge cakes with 100% sugar substitutes were processed at constant regime of baking concurrent with that of the control sample, which according to the technological instruction was baked for 30 min at 180 °C (Figure 1).

Each sponge cake batter of 75 g was poured out into metallic forms and baked in an electric oven at 180°C for 30 min. The sponge cakes were stored at standard conditions (at temperature of 18°C and 75 % relative humidity). The humidity and the temperature were kept constant by means of a desiccator supplied with a psychrometer, and put in a thermostat with an accuracy of ±0.5°C.

Table 1

Sponge cake batters formulations

Ingredients	Amount based on batter weight:	
	Control sample	With 100% sugar substitutes
Yolk of egg, [%]	13.35	13.35
White of egg, [%]	29.88	29.88
Granulated sugar, [%]	25.90	-
Wheat flour, [%]	30.88	27.89
Coconut sugar, [%]	-	19.92
Mesquite flour, [%]	-	5.98
Coconut flour, [%]	-	2.99

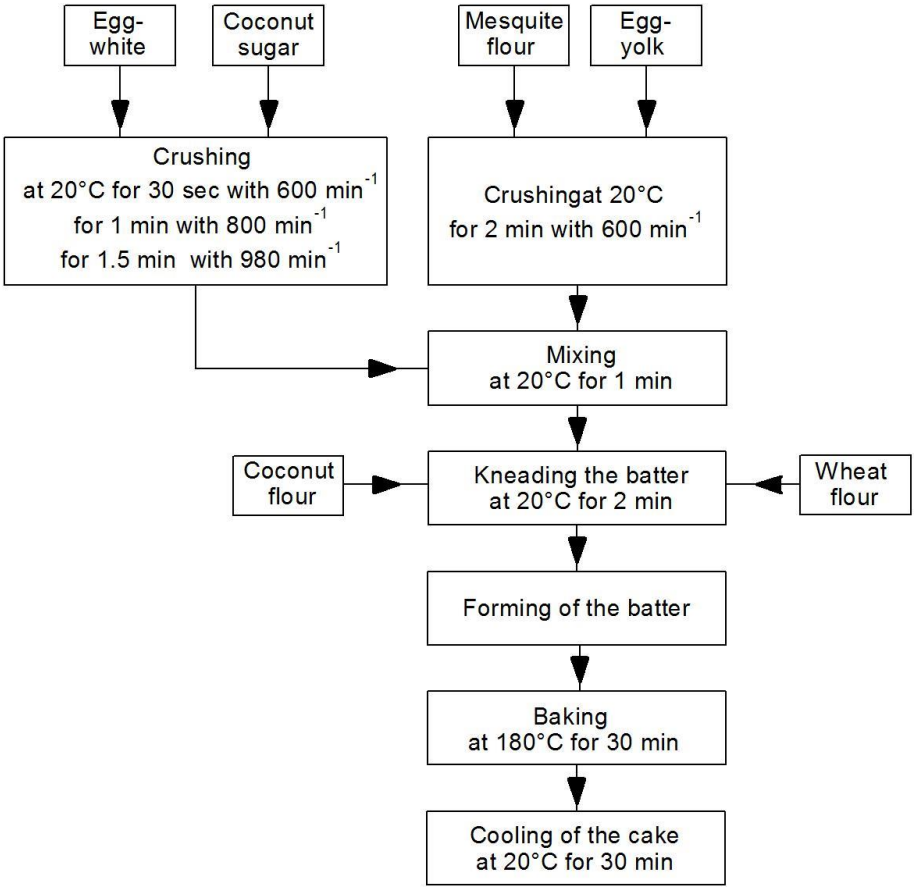

Figure 1. Technological scheme production of sponge cake with sugar substitutes

Physical characteristics of the batters and sponge cakes

The specific gravity of the sponge cake batter was calculated by dividing the weight of a standard batter cup to the weight of an equal volume of distilled water at batter temperature (20.0±0.5ºC) [16]. The physical characteristics of the sponge cakes were determined 2h after baking. Volume was measured by the small uniform seed displacement method [17], and porosity was assessed according to Baeva, *et al*., 2012 [18]. The porosity of the sponge cake was defined as the ratio of the volume of air-pockets in the cake crumb to the volume of the crumb. Porosity determination was made using a cylinder driller, a device of Zhuravljov. The specific volume was expressed as the ratio of the sponge cake volume to its mass. The water-absorbing capacity of the sponge cake was measured by the extent of biscuit swelling according Baeva, *et al*., 2012 [18]. The density was expressed as the ratio of the sponge cake mass to its volume according to Ho et al., 2013 [19].

Baking loss of was calculated by following formula after measuring batter mass (BM) and cake mass (CM) according to Hathorn et al., 2008 [20]:

$$\text{Baking loss} = \frac{\text{BM} - \text{CM}}{\text{CM}} \cdot 100$$

where: BM - batter mass; CM - cake mass.

Measurement of color of sponge cakes

The instrumental measurement of the cakes color was carried out with a colorimeter and the results were expressed in accordance with the CIELAB system. Color was measured at four predetermined places of the sponge cakes crust and crumb. The parameters determined were L* (L* = 0 [black] and L* = 100 [white]), a* (–a* = greenness and +a* = redness), b* (–b* = blueness and +b* = yellowness). Colorimeters give measurements that can be correlated with human eye-brain perception, and give tristimulus (L*, a* and b*) values directly.

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

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

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

where:"0" – control cake; "1" – cake with mesquite.

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

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

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

$\Delta E^* > 3$ color differences are obvious for the human eye [21, 22].

Chemical composition and energy values

The total moisture content in the cake (2 h after baking) was determined using the AACC method 44–15.02 [23] after drying out in an oven at 105 °C to constant weight. The measurements were done in triplicate and the mean values were presented. The total, soluble and insoluble dietary fibre content was determined by ISO 5498:1999, using the total dietary

fibre assay kit TDF 100A (Sigma-Aldrich) and the instructions provided by the manufacturer. Protein was determined by the Kjeldahl method by ISO 20483:2013. A multiplication factor of 6.25 was used for the calculation of protein content. The total carbohydrate content was estimated according to the spectrophotometric method of Dubois et al. (1956). In brief, 0.1 ml of each extract was mixed with 1 ml of 5% phenol and 5 ml of sulphuric acid. The samples were then placed in a water bath at 30 °C for 20 minutes. The absorbance was measured at 490 nm against a blank that was prepared using the same process as that used for distilled H_2O. The fat content of the cakes was determined according to ISO 11085:2015. The energy values were obtained by the Atwater and Bryant method, using the conversion factors of 4, 9, 4 and 2 kcal/g for protein, fat, carbohydrate and dietary fiber, respectively [25]. Nutritional value of 100 g was determined according to Regulation (EU) № 1169/2011 of the European Parliament and of the Council.

Microbiological analysis

The microbiological analyses were carried out according to the Bulgarian State Standard. Analyses for total plate count (TPC) (ISO 4833-1: 2013), molds and yeasts (ISO 21527-2: 2011), coliforms (ISO 4831: 2006), Salmonella species (ISO 6579-1:2017) and coagulasepositive staphylococci (ISO 6888-1: 2000) were also conducted. Total plate count (TPC) in 1 g of sponge sample; the total number of molds and yeasts in 1 g of sponge sample; coliforms in 1 g of sponge sample; *Salmonella* species in 25 g of sponge sample and coagulase-positive staphylococci in 1 g of product were determined.

Statistical analysis

All experiments were performed in triplicate. The data were analyzed and presented as mean values±standard deviation. Statistical analysis was conducted using the Statgraphics Centurion XVI Version 16.2.04 software (Statpoint Technologies Inc., USA). The analysis of variance technique, incl. Lavene's test (ANOVA) and Multiple Range Test were used to determine significant differences at 95 % confidence level ($p < 0.05$).

Results and discussion

Physical characteristics of the sponge batters and cakes

The addition of coconut sugar and mesquite flour mix in sponge cakes improves their physical characteristics (Table 2). Specific gravity in cake batter provides an indication of the total air holding capacity of the batter. Low specific gravity values indicate good incorporation of air, yielding a higher final volume after baking; however, many other factors also affect this quality parameter. The difference in respect the specific volume between the control cake-sample and the sponge cakes with sugar substitutes is minimal. Specific volume of cakes varied between 2.92±0.10 cm^3/g and 3.13±0.11 cm^3/g. According to Herranz et al., 2016 [26] all cheackpea flour-based muffins had significantly lower specific volume than the control. Volume of cake indicated the ability of batter to expand and incorporate gas during the baking process. In this studying the volume of the cake with sugar substitutes was smaller than this of cake control (219.00±2.07 cm^3). The greatest porosity was observed in the cake control (63.23±1.30%). The water-absorbing capacity of the cake with coconut sugar and mesquite flour (315.60±3.08%) is the lowest than that of the cakes cake control.

Table 2

Physical characteristics of the sponge batters and cakes

Physical characteristics[a]	Sponge cake types	
	Control sample	With 100% sugar substitutes
Specific gravity (for batter)[b]	0.71±0.02[c]	0.70±0.02[c]
Volume, cm^3	235.00±2.02[c]	219.00±2.07[d]
Specific volume, cm^3/g	3.13±0.11[c]	2.92±0.10[c]
Porosity, %	63.23±1.30[c]	61.05±1.20[c]
Water-absorbing capacity, %	319.68±3.12[d]	315.60±3.08[d]
Density, g/cm^3	0.32±0.11[c]	0.34±0.10[c]
Baking loss, %	17.55±0.69[c]	15.27±0.53[d]

[a] The values are mean±SD ($p < 0.05$).

[b] The temperature of the batter is on the average 20.7±0.5 °C.

[c-d] The values in a line with identical letters do not different statistical significantly ($p < 0.05$).

Cake density, which is defined as weight of unit cake volume (g/cm^3), increased by add coconut sugar and mesquite flour mix. There were no differences between density of control cakes and sugar substituted cakes, likewise porosity and specific gravity values of cakes ($p>0.05$).

Gas formation during baking caused an increase in vapor pressure, which was likely due to the expansion of liquids when heat was applied to the batter. The loss of gas during baking is called 'baking loss' [27]. Baking losses of all the samples were in the range of 15.27–17.55%. Sugar substituted cakes had less baking loss and were statistically different from control. Mohamed et al., 2012 [8] reported that green banana flour components which had high water binding capacity, especially insoluble fibers (lignin, cellulose, hemicellulose), could cause water intake from other ingredients in product formulation. They also reported [28] that high percentage substitution of green banana flour leads to high water intake from other ingredients in product formulation, and it effects quality characteristics of dough and final product such as volume, hardness and colour negatively. In other study, decrease of baking loss with increasing GBPF substitution level may be attributed to high water absorbing capacity (4.91-5.88 g water/ g dry matter) reported by Alkarkhi et al., 2011 [28] which is a functional characteristic of green banana flour.

Color characteristics

The effects of sugar substitutes addition on the color characteristics of sponge cakes are presented in Figure 2 and Figure 3. The results were expressed by L*, a* and b* values corresponding to lightness, redness, and yellowness, respectively. Significant differences of the crust and crumb colors were observed between the control cake and the cake substituted with sugar substitutes ($P<0.05$).

Crust color of cakes. The brownish color of crumb in composite breads is not due to the development of Maillard products, but probably to enzymatic reaction products since in the stages of dough preparation the darkening of the dough with the presence of mesquite flour was already observed [29]. In this way, during dough preparation in the presence of water, browning enzymatic reactions may occur. The lightest samples (highest L* values) were control cake (58.49±1.23) present in Figure 2. The control have the highest values of a* and

b* indicating a significantly brighter and more saturated yellow color. The lightness, a* and b* values for control were significantly different from those of the cake with sugar substitutes. According to these results, cakes with sugar substitutes – coconut sugar and mesquite flour where the ΔE* was appreciable by the human eye (ΔE*> 3).

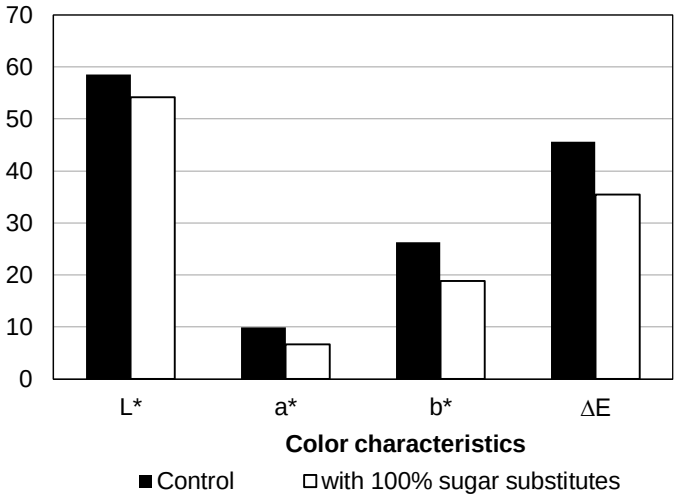

Figure 2. Crust color values of sponge cakes

Cake crust of control sample had the highest values of L* (58.46±2.25), a* (9.56±0.62) and b* (25.31±0.82). The brownish color of crust is mainly due to the development of products of non-enzymatic browning reaction (Maillard), favored by the loss of moisture and high temperatures during baking in the presence of sugars and proteins.

Crumb color of cakes. The variations in the crumb color of the cakes with sugar substitutes as sugar replacer were similar to the variations in crust color (Figure 3). The crumb of cake with coconut sugar and mesquite flour mix was brownish and darker than cake control crumb. The cake control was the lightest and the b* values showed that this sample had a brighter color. According to these results, the cake with sugar substitutes where the ΔE* was appreciable by the human eye.

The brownish color of crumb in composite breads is not due to the development of Maillard products, but probably to enzymatic reaction products since in the stages of dough preparation the darkening of the dough with the presence of MF was already observed. The polyphenol content of MF was previously reported by several authors [30-31] and even though there are no recent reports of polyphenol oxidase activity in mesquite, the presence of this enzymatic activity in many legumes is well known [32]. In this way, during dough preparation in the presence of water, browning enzymatic reactions may occur.

Generally, crumb color of the cakes is affected by the ingredient used and its formulation [33].

The brownish color of crumb in composite breads is not due to the development of Maillard products, but probably to enzymatic reaction products since in the stages of dough preparation the darkening of the batter with the presence of mesquite flour was already observed.

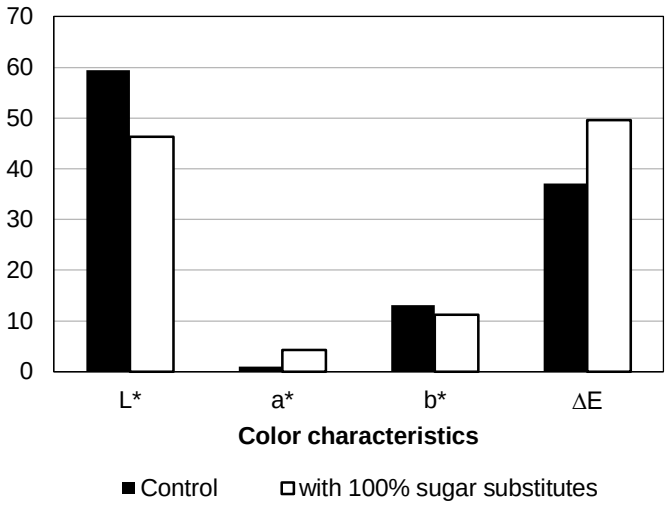

Figure 3. Crumb color values of sponge cakes

The difference in chemical composition of sugar and coconut sugar and mesquite flour mix might provide different colors of the new cake.

Chemical composition and energy value of sponge cakes

The results of chemical composition and energy value of sponge cakes with functional ingredients are presented in Table 3.

Table 3

Chemical composition and energy value of sponge cakes (100 g product)

Basic chemical composition and energy value	Type of sponge cakes	
	Control	With 100% sugar substitutes
Total moisture, [%]	28.55 ±0.04[b]	30.00±0.01[c]
Protein, [%]	14.09±0.10[b]	21.01±0.16[c]
Fat, [%]	6.89±0.03[b]	5.66±0.32[b]
Carbohydrate[a], [%]	58.21±0.31[b]	23.50±0.20[c]
Total dietary fibre, [%]	2.21±0.28[b]	9.50±0.21[c]
– Insoluble dietary fibre, [%]	1.61±0.07[b]	6.77±0.08[c]
– Soluble dietary fibre, [%]	0.60±0.03[b]	2.73±0.09[c]
Energy value, [kJ/100 g] [kcal/100 g]	 1449.58 346.79	 878.58 209.98

[a] "Carbohydrate" any carbohydrate which is metabolized by the human body with the exception of dietary fibre according Regulation (EU) № 1169/2011.

[b-c] The values in a line with identical letters do not different statistical significantly ($p < 0.05$).

The cake with 100% sugar substitutes was with the highest level of moisture (30.00%), and the control cake was with the lowest moisture content (28.55%). The sample with 100% sugar substitutes (21.01%) was characterized with the highest protein content, while the lowest protein content was found in the cake control (14.09%).

The highest fat content was defined in the sample control (6.89%) and the lowest content was in the cake with coconut sugar and mesquite flour (5.66%). The highest percentage of carbohydrate was determined in the control (58.21%), as with the lowest content was the cake with coconut sugar and mesquite flour (23.50%). According to the obtained results the carbohydrate content decreased with the addition of the natural sugar substitutes. The results indicated that there was a significant increase in the total dietary fibre content in sponge cakes incorporated with natural sugar substitutes. The highest amont of total dietary fibre had cake with 100% sugar substitutes (9.50%), while it was 2.21% for control cake. By forming viscous solution, soluble fibre slows intestinal transit, delays gastric emptying, and reduces glucose and sterol absorption by the intestine. It is important to note that sponge cake with natural sugar substitutes could be tagged as foods and could support the claim "with high content of dietary fiber", according to the provisions of FAO/WHO guidelines (Codex Alimentarius Commission & FAO, 2009) [34] because they exceed the 6 g of TDF per 100 g of product. The energy value of sponge cakes control is 346.79 kcal/100g of product, as the cake with coconut sugar and mesquite flour being the lowest – 209.98 kcal/100g of product, with 37% lower than the control cake. Bigne et al., 2018 [3] reported that the high level of fibre in mesquite flour led to changes in the textural properties of dough, as a consequence of an inferior development of the gluten network. Higher levels of added mesquite flour led to dough with increased consistency and less cohesiveness, where a disruption of the gluten matrix was observed.

The most relevant nutritional aspect is related to the fibre content of cake. With only 30% replacement of sugar by mesquite flour, total dietary fibre content increased more than twice, reaching a value of 9.50 g/100g.

Microbiological analyses

Microbiological spoilage is often the major factors limiting the shelf life of bakery products. Spoilage from microbial growth causes economic loss for both manufacturers and consumer. These losses could be due to many individual cases such as, packaging, sanitary practice in manufacturing, storage conditions and product turnover. Yeast problems occur in bakery products. Contamination of products by osmophilic yeasts normally results from unclean utensils and equipment. Therefore, maintaining good manufacturing practices will minimize the contamination by osmophilic yeasts. According to Malkki & Rauha [35] mold growth on bakery products is a serious problem that results in economic losses. Furthermore, losses of products due to mold spoilage are between 1 and 5 per cent depending on the type of product, season, and the method of processing. Mold spores are generally killed by the baking process in fresh bread and other baked products [36]. Therefore, for bread to become moldy, it must be contaminated either from the air, bakery surfaces, equipment, food handlers or raw ingredients after baking during the cooling, slicing or wrapping operations. This means that all spoilage problems caused by molds must occur after baking [37]. The mold spore counts are higher in the summer months than in the winter due to airborne contamination in the warmer weather and more humid storage conditions. Furthermore, moisture condensation on a product's surface, due to packaging prior to being completely cooled, may be conductive to mold growth [38].

The results of total plate count (TPC) and yeast and mould count of sponge cakes are presented in Table 4. No pathogenic bacteria such as coagulase-positive staphylococci in 1 g of the samples *Salmonella* spp. in 25 g of the samples and fecal coliforms in 1 g of the samples, respectively, were not detected.

Table 4

Microbiological characteristics of the sponge cakes

Microbiological characteristics	Control	With 100% sugar substitutes
Coliforms, [CfU/g][1]	ND[2]	ND
Salmonella spp.in 25 g	ND	ND
Coagulase-positive staphylococci, [CfU/g]	ND	ND
Total plate count, [CfU/g]	0	0
Molds and yeast, [CfU/g]	0	0

[1] CfU/g – Colony forming Units per gram
[2] ND = Not detected

Up to the first day of storage at room temperature, no evidence of mold was detected on the samples.

The study of Soltandelal et al., 2010 showed that contamination of fresh dough to molds, yeasts, Enterobacteriaceae, Bacillus and Staphylococcus differ from 50 to 83%, respectively [39].

According research of some autors [41–42] cross contamination is one of the reasons for contamination of cakes by molds. Most of the contaminated factors are destroyed in process because of high temperature of cooking process, so Probably one of the reasons being cake samples free from contamination or in accepted levels in our factory were the worker's personal hygiene. In addition to the importance of personal hygiene, additional activities to promote health and quality level of these products and improve them to global standards and excellent sanitary process must be done.

Conclusion

1. The flour obtained from the pods of *Prosopis alba* (mesquite flour) demonstrated to be a versatile ingredient to be incorporated in “cake” formulations. The sponge cake made with composite coconut sugar and mesquite flour exhibited fairly good technological characteristics.
2. A remarkable aspect is that from a functional and nutritional point of view, these cakes contained significantly higher levels of dietary fiber than the traditional bakery products prepared with sugar.
3. The results confirm the adaptability of mesquite flour to be incorporated in different cakes formulations rendering healthier distinctive products.

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Effect of plasmochemically activated aqueous solution on process of food sprouts production

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Abstract

Introduction. The effect of plasmochemically activated aqueous solutions on the process of production of food sprouts of legume crops is studied. The paper presents the characteristic of activated aqueous solutions, their effect on the germination process and microbiological status of sprouts.

Materials and methods. Grain of legumes (peas, soybeans, chickpeas, kidney beans, lentils, beans, lupines) was sprouted with the use of plasmochemically activated aqueous solutions as an intensifier of germination. In order to determine the amino acid and vitamin composition of sprouts, the method of ion-exchange liquid column chromatography was used.

Results and discussion. Legume germination energy and capacity increased with the use of plasmochemically activated aqueous solutions. At the optimal concentration of peroxides equal to 400 mg/l, the germination energy increased by 10–12%, and the germination capacity featured growth by 8–10%. Monitoring of the sprout length showed the increase in length from 6 to 14 mm. Control of weight of sprout biomass also demonstrated positive results, that is, 4–16 % sprout weight gain, depending on the crop (peas −8%; soybeans −10%; chickpeas − 7%; kidney beans −14%; lentils − 4%; beans − 16%; lupines − 10%).

Study of the microbiological status of sprouts showed stable disinfecting action of plasmochemically activated aqueous solutions owing to the presence of hydrogen peroxide in their composition (100–700 mg/l). No pathogenic microflora was recorded on the sprouts treated with plasmochemically activated aqueous solutions with the peroxide concentration of 400 mg/l and more (Aspergillus, Alternaria, Penicillium, Fusarium, Mucor).

Owing to the usage of plasmochemically activated aqueous solutions, legume sprouts demonstrated the increase in the content of B group vitamins (B_1, B_2, B_3, B_6, B_{12}), as well as PP, E, C, A. The number of amino acids increased by 4–52%. It is explained by more active development of legume sprouts, while using the intensifier of germination, i.e. plasmochemically activated aqueous solutions.

Conclusions. Usage of plasmochemically activated aqueous solutions is a promising process technology for obtaining high-quality product rich in amino acids and vitamins.

Introduction

Sprouts obtained from different crops have a specific set of nutrients, vitamins and microelements [1]. Grain crops are the most popular ones for germination [2]. The important technological aspect is the expansion of the range of crops for obtaining of food sprouts and their inclusion in the human diet [3].

The promising areas of intensification of the traditional technology for producing food sprouts are focused on creation of the favorable conditions for the germination of grain material and reduction of the duration of the process of sprout production by optimization of parameters of soaking and germination [4]. However, the modern intensifiers have a chemical nature and can adversely affect the finished product quality.

In order to intensify the technology for obtaining of food sprouts, a number of methods to activate the germination of grain material are used [5]: physical methods (ultrasonic waves, ionizing radiation, electromagnetic fields, incoherent red light) [6], chemical methods (diammonium phosphate, potassium bromide), physical-chemical methods (plasmochemical treatment of aqueous solutions, usage of ozonized aqueous solutions) and microbiological methods (enzyme preparations) [7].

Popular methods of intensification of the food sprouts' production technology include the use of germination bio-stimulants [8], among which organic acids are the most common (gibberellic acid, lactic acid, ferulic acid, indole acetic acid) [9]. Application of the above acids was studied in the malt technology only; no information of that kind is available for the production of food sprouts.

Organic acids mentioned below are used in the process of grain material germination: malic acid, racemic acid, citric acid [10], succinic acid, nicotinic acid, folic acid and their complexes [11]. Fruit acids are widely used in the germination process [12]. However, all these intensive technologies involve chemical compounds in the germination process, which does not allow obtaining completely safe product [13].

High quality of the obtained germinated grain raw materials is an important aspect in the implementation of intensive germination technologies [14]. It is of particular importance for the production of germinated grain [15], since it is used fresh. Furthermore, considerable attention is given to the microbiological status of food sprouts because of its effect on the quality and duration of storage [16]. This is due to the fact that in the process of germination a variety of microflora, including pathogenic one, develops on the grain surface [17]. Therefore, the prospects of finding new multi-purpose intensifiers of the grain germination in order to obtain high-quality food sprouts represent an urgent problem of the grain processing industry [18]. Versatility and safety of the germination intensifiers is of the utmost importance in this context [19]. So, the search for the intensifier mentioned above is a high-priority issue.

The usage of plasmochemically activated aqueous solutions [20] in the food industry [21] and in the production of malts for various purposes was studied before. Our task was to determine the effect of activated solutions on the process of obtaining the food sprouts and their microbiological status [21].

Activation of water and aqueous solutions by plasma-chemical treatment is the first step to using the properties of water without involvement of the artificial foreign chemicals of the different origin [20]. The resulting activated water has a specific composition. Reaction products, which determine the reactivity of such water, are the most easily detectable ones. This primarily applies to hydrogen peroxide and superoxide compounds, excited particles and radicals, which play an important role in redox processes.

So, all processes which occur during activation are processes taking place directly in the aqueous medium [22]. Reactogenic properties of plasmochemically treated water represent priority subject for the scientists, because the properties of water arising after activation can be a starting point in the development of a new trend in nanotechnologies [23]. Plasmochemically activated water has antiseptic and antibacterial properties [24]. This water represents a cluster structure after plasma treatment and can exhibit some new properties, previously little studied, but important from the practical point of view [25, 26]. A special role in this case is given to studying of the influence of activated water on the parameters of some processes in food, biochemical and biotechnological productions [27]. One of such processes is the obtaining of food sprouts of legume crops.

Research *objective* is the determination of the effect of plasmochemically activated aqueous solutions on the process of production of food sprouts.

In order to achieve the above objective, the following *tasks* were solved: studying of the legume germination energy and capacity; control of the length of legume sprouts during germination and weight of their biomass; studying of the microbiological status of sprouts; determination of the content of amino acids and vitamins in sprouts; selection of the optimal parameters of plasma-chemical activation of aqueous solutions.

Materials and methods

Materials

The legume crops (peas, soybeans, chickpeas, kidney beans, lentils, beans, lupines) were taken as the grain raw materials for germination (production of sprouts). Plasmochemically activated aqueous solutions acted as the intensifier of the process of germination [20].

Four analytical groups were selected for research from all legume crops: 500 pcs. each for small legumes and 250 pcs. each for the larger ones [8].

Plasma-chemical activation of the aqueous solutions

Water was activated using the laboratory plasma-chemical unit (Fig. 1). Tap water was activated in plasma discharges of reduced pressure with the voltage of 1000–1200 V and current of 30.0–200.0 mA with the subsequent transition (with electrical conductivity increase) to the mode of non-equilibrium contact plasma with the following parameters: voltage from 400 to 600 V and current up to 150 mA. The content (concentration) of hydrogen peroxide in the activated water was determined by iodometry [28].

The unit works as follows [20]: input voltage is supplied to step-up transformer; AC voltage from the secondary winding of the transformer is applied to the bridge rectifier and further pulsating DC voltage through the ballast resistor is supplied to the reactor electrodes. Additionally, the reactor anode is connected with the ignition device, which generates the pulses with the amplitude of up to 15 kV and duration of up to 1.5 ms. The pulses are rigidly synchronized with the phase of the pulsating voltage. At the time of formation of ignition pulse, breakdown of the vacuum space (created by pumping the gaseous phase from the reactor by the vacuum pump) occurs between electrodes of the reactor. There is a sharp drop in resistance; as a result, the anode current begins to flow, creating a discharge. The voltage of burning of the discharge is almost constant, at the level of 750-900 V, depending on the degree of gas liquefaction within the reactor. The magnitude of current of the discharge gap

is conditioned by the plasma resistance and the value of voltage applied to the system plasma discharge – ballast regulator. The voltage value is regulated according to the phase method, i.e. average value of the anode voltage supplied to the reactor depends on the phase of pulsating voltage at the anode and the moment of feeding of the ignition pulse. Plasma occurs at the time of ignition and goes out at the end of the anode voltage ripple. The repetition frequency in the process is 100 Hz. Regulation of the discharge current used in the device is carried out by changing the ignition moment relative to the phase of the anode voltage ripple using a synchronizing device. In this case, the reactor itself acts as a power-regulating unite. Parameters of the plasma discharge are recorded using the equipment of M4200 type, class 4.0.

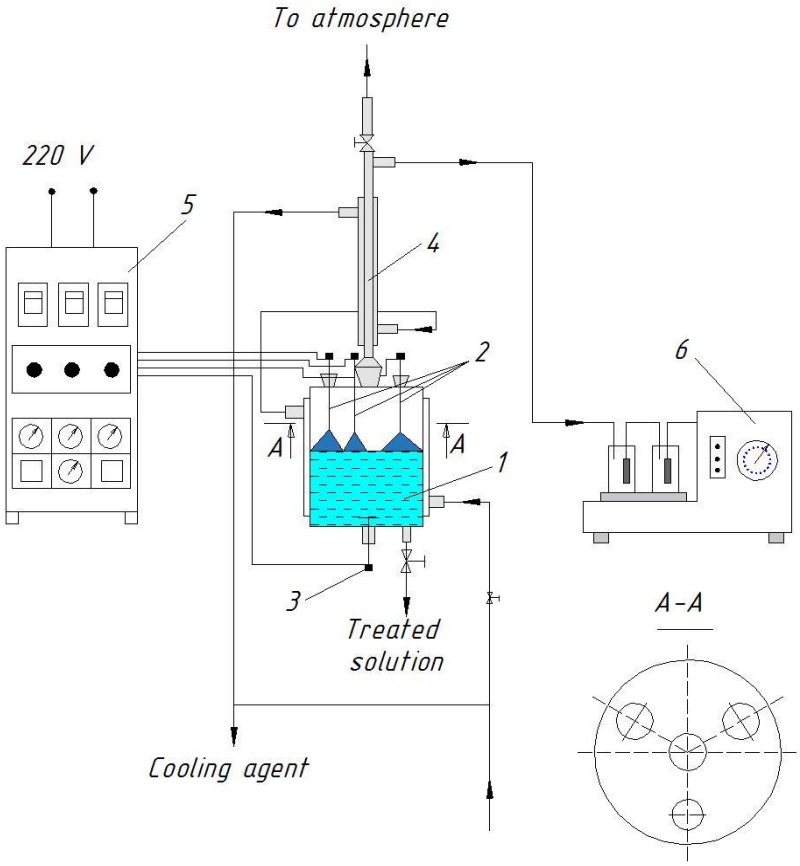

Figure 1. Diagram of the laboratory three-arc plasma-chemical unit:
1 – reactor; 2 – anodes; 3 – cathode; 4 – reflux condenser;
5 – power supply; 6 – vacuum pump.

Characteristic of the activated water used as an intensifier of germination during soaking of legumes is given in Table 1.

Table 1

Characteristics of water activated by non-equilibrium contact plasma

Experiment	Water	Activation time, minutes	Concentration of hydrogen peroxide, mg/l
1 (control)	Tap water	-	-
2	Activated water	10	300
3	Activated water	20	400
2	Activated water	30	600
4	Activated water	40	650
5	Activated water	60	700

Sprouting of legumes with the use of plasmochemically activated aqueous solutions

Grain of legumes was sprouted in the laboratory malt house representing a set of plastic containers covered with the layer of filter paper [29]. The grain material was treated with plasmochemically activated aqueous solutions (with the concentration of peroxides of 300–700 mg/l) as follows: legume crops prepared for germination were saturated with plasmochemically activated solutions in two stages. Pre-soaking was carried out for 4 hours at the temperature of 18-20 °C [12]. At the end of the period, the nutrient solution was drained, and the grain was held for 18 hours without access of the liquid. The activated solution of the similar concentration was used during repeated soaking. Air-and-water soaking was carried out for 26 hours till complete saturation of the grain with the preparation [11]. Germination was performed for 3-15 days at the temperature of 17–21°C, with the periodical moistening and shaking of the grain layer of maximum 45–55 mm high, in order to evenly distribute the liquid and prevent agglomeration of the mass. Depending on the process needs, the final stage of the process was cooling, grinding or drying of sprouts [8].

Method for determination of the legume germination energy and capacity, length and weight of biomass of sprouts

Germination energy and capacity was determined for establishing the amount of legumes capable of forming the normally developed sprouts [30]. Together with the germination capacity, we determined the energy of legumes' germination, characterizing the rate of germination and sprout vigor. Capacity and energy of germination was expressed as a percentage of normally sprouted grain to the total quantity. Energy and capacity of germination of the grain material was determined, accordingly, on the expiry of 72 hours and 120 hours after completion of grain soaking [8]. These values were expressed in % to the total quantity of grains in the test sample. Effectiveness of selected intensifiers of growth was compared to the control, i.e. the grain not subjected to any chemical treatment. Besides, the length of sprouts was also measured to monitor the activity of grain germination and speed of sprout formation during 15 days. In parallel with it, the obtained biomass was weighed. All experiments were performed five times.

Method for determination of microbiological status of grain material in the process of germination

The change in microbiological status of the grain material was observed under the microscope MBS-56, and inoculation of the nutrient medium with the wipe samples was made with the further counting of colonies of microorganisms [31].

Analysis of the content of amino acids and vitamins

In order to determine the nutrition value of the obtained product, we analyzed the amino acid content in legume sprouts, using for this purpose the method of ion-exchange liquid column chromatography [32]. The process of determination was performed on the automatic analyzer of amino acids T339 (Prague, Czech Republic) [9]. The vitamin composition of sprouts was also determined using ion-exchange liquid column chromatography and other standard methods [8].

Results and discussion

Studying of energy and capacity of germination of legume crops with the use of plasmochemically activated aqueous solutions

Germination energy and capacity are the important indicators of the process of legumes' germination (Table 2).

Table 2

Energy and capacity of germination of legumes with the use of plasmochemically activated aqueous solutions

Crops	Control	Peroxide concentration in plasmochemically activated aqueous solutions, mg/l				
		300	400	600	650	700
Germination energy						
Peas	80	85	92	89	86	83
Soybeans	80	85	91	88	85	84
Chickpeas	81	86	91	89	86	84
Kidney beans	80	86	90	87	85	83
Lentils	81	86	92	89	86	84
Beans	80	85	90	87	86	83
Lupines	80	84	91	88	84	82
Germination capacity						
Peas	91	94	99	96	94	93
Soybeans	90	94	100	97	96	92
Chickpeas	91	93	99	95	94	92
Kidney beans	92	95	100	96	95	92
Lentils	91	94	99	94	92	91
Beans	90	94	99	95	93	91
Lupines	91	95	100	96	94	92

We observed the higher activity of germination in the experimental analytical groups compared to the control, which indicated the possibility of using plasmochemically activated water for intensification of the germination of legumes. A similar tendency was demonstrated by all crops under study. So, the germination energy and capacity increased, correspondingly, by 10-12% and 8-10%. Optimal concentration of peroxides in the activated solutions was equal to 400 mg/l. It is explained by the fact that activated water accelerates the inflow of moisture to the grain and, as a consequence, nutrients are transferred from the endosperm to the germ, stimulating its awakening to active life; it can accelerate the accumulation of cytolytic, proteolytic and amylolytic enzymes.

The chaotic motion of ions [27] in the activated water allows accelerating the diffusion of water into the grain due to more active inflow of charged particles to the grain surface. This aspect confirms the fact that with the use of activated water as a moisturizing agent, due to its specific composition, moisture is more actively transported into the grain. That is, the activated water quickly diffuses into the grain.

Hull of the grain contain the germination inhibitors impeding the grain germination at rest [33]. During soaking, they should be leached and removed. Since the activated water has an alkaline nature, with peroxide and superoxide compounds in its composition, their usage accelerates the leaching of substances, which inhibit the growth. Furthermore, the alkaline environment promotes leaching of tannins, bitter substances and proteins from the hull [18]. In addition, the alkaline solution promotes additional washing of the grain. Hydrogen peroxide being a part of the activated water acts as an oxidant and, as a result, improves the grain purification. On the other hand, it stimulates the grain germination at the time of oxygen release. The alkaline environment does not have any significant negative impact on the subsequent quality of sprouts [18].

Water is absorbed mainly through the vessels, which exit at the basal end of the grain [18]. After penetration of water into the grain, transfer of water from the endosperm to the germ begins. Migration of charged particles in the grain results in the inflow of negatively charged particles to the germ and outflow of positively charged particles. These processes increase the permeability of grain structures to water and nutrients. The capillary condensation occurs quickly, and the activated water is absorbed with the formation of condensate in the grain capillaries. In parallel with the increase in grain moisture, activity of amylases, ribonucleases and phosphatases (which are further broken down in the absence of oxygen) is growing [34]. Activated water contains hydro-peroxide radicals, which promote the oxygen formation leading to the further increase in the content of the above enzymes and more active breakdown of endosperm components. As a result, the intensification of legume germination can be observed. Therefore, duration of the technological process of obtaining the sprouts can be significantly reduced.

When we compare the results with the other studies [8, 35], it is necessary to note more active progress of the germination process, namely, increase in energy and capacity of germination by 2-3% compared to other intensifiers, representing undeniably positive result.

Studying of the change of length and weight of biomass of legume sprouts with the use of plasmochemically activated aqueous solutions

In order to monitor the change in the length of sprouts, they were measured in 72 hours after the start of the germination process. The averaged data by analytical groups are given in Table 3.

Table 3

Change in the length of legume sprouts with the use of plasmochemically activated aqueous solutions, mm

Crop	Control	Peroxide concentration in plasmochemically activated aqueous solutions, mg/l				
		300	**400**	**600**	**650**	**700**
Peas	17	22	31	29	25	22
Soybeans	18	23	31	30	28	24
Chickpeas	19	23	32	31	26	24
Kidney beans	30	34	41	39	37	34
Lentils	7	11	15	14	12	11
Beans	42	48	54	52	50	48
Lupines	12	15	18	17	16	14

After analysis of our findings, we can make a conclusion about more intensive development of sprouts in all legume crops with the use of plasmochemically activated aqueous solutions during soaking. The optimal concentration of peroxides in the solutions was also equal to 400 mg/l, so the activation modes for aqueous solutions were chosen correctly.

Dynamics of sprout formation was identical for all legume crops. Presented experimental data show that activation of growth processes with the use of plasmochemically activated aqueous solutions is observed absolutely in all legume crops under study.

Quantity of sprouts (biomass) [35] obtained after completion of the cycle of all process operations is an important indicator of the industrial production. The yield of the finished product, namely, legume sprouts with the use of plasmochemically activated solutions ranged from 4–16% depending on the legume crop (peas −8%; soybeans −10%; chickpeas −7%; kidney beans −14%; lentils −4%; beans −16%; lupines −10%). Therefore, the proposed intensive technology of sprout production will allow obtaining a larger amount of food product, which is a positive characteristic of the process.

Studying of microbiological status of legume sprouts after treatment with plasmochemically activated aqueous solutions

Plasmochemically activated aqueous solutions exhibit antiseptic properties, which further reduces the microbial contamination of sprouts and has a positive effect on the microbiological indicators of the finished product [20]. So, the sprouts were further treated with plasmochemically activated solutions for disinfection (Table 4).

Table 4

Effect of plasmochemically activated aqueous solutions on the pathogenic complex of legume sprouts, % of infected sprouts

Exposure, minutes	Infection with fungal microflora	Peroxide concentration in plasmochemically activated aqueous solutions, mg/l							
		0	100	200	300	400	500	600	700
10	Aspergillus	98	70	30	8	0	0	0	0
	Alternaria	30	28	10	5	0	0	0	0
	Penicillium	25	7	5	2	0	0	0	0
	Fusarium	6	2	1	0	0	0	0	0
	Mucor	31	17	12	5	0	0	0	0
20	Aspergillus	99	42	15	5	0	0	0	0
	Alternaria	31	14	6	3	0	0	0	0
	Penicillium	25	4	3	1	0	0	0	0
	Fusarium	6	1	0	0	0	0	0	0
	Mucor	39	11	4	2	0	0	0	0
30	Aspergillus	99	19	8	2	0	0	0	0
	Alternaria	32	6	3	1	0	0	0	0
	Penicillium	26	2	1	0	0	0	0	0
	Fusarium	6	1	0	0	0	0	0	0
	Mucor	42	7	3	1	0	0	0	0
40	Aspergillus	99	9	3	1	0	0	0	0
	Alternaria	33	2	1	0	0	0	0	0
	Penicillium	26	1	0	0	0	0	0	0
	Fusarium	6	0	0	0	0	0	0	0
	Mucor	43	3	1	0	0	0	0	0
50	Aspergillus	99	3	1	0	0	0	0	0
	Alternaria	33	1	0	0	0	0	0	0
	Penicillium	27	1	0	0	0	0	0	0
	Fusarium	7	0	0	0	0	0	0	0
	Mucor	43	2	0	0	0	0	0	0
60	Aspergillus	100	1	0	0	0	0	0	0
	Alternaria	33	1	0	0	0	0	0	0
	Penicillium	27	0	0	0	0	0	0	0
	Fusarium	7	0	0	0	0	0	0	0
	Mucor	43	0	0	0	0	0	0	0

Consequently, when using the activated aqueous solutions the quantity of infected sprouts is significantly reduced. At the concentration of peroxides of 400 mg/l, pathogenic microorganisms are completely absent. One possible mechanism of action of the activated water on bacteria is the change in outer layers of the cell, which makes the receptors accessible for reactogenic enzymes, such as lysozyme. Free radicals can form a gap in the cell wall, which leads to the loss of selective permeability [31]. Peroxide being a part of the activated water causes the destruction of surface structures and internal membranes in microorganisms [20]. Integrity of the cytoplasmic membrane disrupts the functions of a number of membrane-related enzymes, such as dehydrogenases, and reduces the efficiency of the DNA repair systems. Bactericidal activity of the hydrogen peroxide and activated water is primarily associated with their high oxidation capacity, as well as action of toxic products, which arise during lipid peroxidation [21]. Peroxidation affects the ribosome proteins, causing their destruction. Furthermore, destruction of the membrane structure is promoted by the formed superoxides [20]. The action of the hydrogen peroxide or activated water results in the local destruction of the integral cell wall and disruption of permeability of the bacterial cells in the first minutes of contact. The peculiar feature of the activated water is also the selective ability to directly destroy the pathogenic microflora [36]. Therefore, the result of the use of plasmochemically activated aqueous solutions is the microbiological purity of sprouts [37], which allows consuming them without the additional heat treatment.

Analysis of microbiological indicators of sprouts, compared to the other studies [36,37], allow saying about the stable disinfecting ability of plasmochemically activated aqueous solutions.

Studying of the content of amino acids and vitamins in sprouts obtained with the use of plasmochemically activated aqueous solutions

The vitamin composition of legume sprouts varied with the use of plasmochemically activated aqueous solutions; results are given in Table 5.

Table 5

Average vitamin composition of legume sprouts obtained according to the intensive technology, mg%

Vitamins	Control	Peroxide concentration in plasmochemically activated aqueous solutions, mg/l				
		300	400	600	650	700
B_1	0.620	0.679	0.687	0.680	0.675	0.671
B_2	0.641	0.655	0.669	0.661	0.658	0.652
B_3	1.871	1.879	1.887	1.881	1.875	1.870
B_6	0.535	0.549	0.562	0.550	0.548	0.541
B_{12}	0.511	0.521	0.528	0.520	0.518	0.512
PP	0.303	0.311	0.319	0.314	0.311	0.307
E	1.322	1.333	1.350	1.341	1.339	1.331
C	6.225	6.238	6.265	6.242	6.241	6.235
A	2.591	2.629	2.679	2.654	2.650	2.631

For example, with the use of the proposed process intensifier, the content of vitamins in legume sprouts increased. The maximum quantities of vitamins is observed at the peroxide concentration of 400 mg/l. This is due to the activation of all biological processes in the grain in the course of construction of a sprout, since the formation of a new plant takes place [38]. As the plasmochemically activated aqueous solutions intensify the process of germination and sprout formation, the results are understandable and quite logical.

The content of amino acids in legume sprouts was also studied. The maximum number of amino acids in sprouts is observed at the peroxide concentration of 400 mg/l. So, the number of amino acids with the use of plasmochemically activated aqueous solutions increased. The content has grown by: lysine − 9–18%; histidine − 12–17%; arginine − 6–7%; aspartic acid – 9–10%; threonine − 20–22%; serine − 15–16%; glutamic acid – 4–5%; proline − 5–6%; glycine − 51–52%; alanine − 12–14%; cystine − 50–52%; valine − 27–28%; methionine − 51–52%; isoleucine − 12–14%; leucine − 10–12%; tyrosine − 11–12%; phenylalanine − 14–16%; glutamine − 7–8%. Therefore, compared to the control sample, amino acid content increased by 4–52%. It is explained by more intensive development of sprouts, during which amino acids accumulate more actively [39], since they participate in the formation of the future plant.

Studying of the vitamin and amino acid composition of sprouts compared to the other studies [35, 39] suggests the higher level of vitamins and amino acids in the legume sprouts with the use of plasmochemically activated aqueous solutions. It allows saying about the increased biological value of the finished product.

Conclusions

1. Indicators of germination of legumes were studied with the use of plasmochemically activated aqueous solutions: germination energy and capacity increased, correspondingly, by 10–12% and 8–10%.
2. Monitoring of the sprout length showed the increase in length from 6 to 14 mm. Weight of sprouts increased by 4–16 %, depending on the crop.
3. Study of the microbiological status of sprouts showed the pronounced disinfecting action of plasmochemically activated aqueous solutions with peroxide concentration of 400 mg/l and more.
4. Study of the amino acid composition demonstrated the higher content of amino acids in sprouts (by 4–52%). We also observed the increase in the content of vitamins B_1, B_2, B_3, B_6, B_{12}, PP, E, C, A in legume sprouts with the use of plasmochemically activated aqueous solutions.
5. Plasmochemically activated aqueous solutions with peroxide concentration of 400 mg/l are optimal for use in the process of legume sprouts' production. Usage of the proposed intensifier allows obtaining high-quality product with the increased content of vitamins and amino acids in the shorter time. In addition, the resulting product is free of pathogenic microorganisms.

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Effect of non-malted barley on low alcohol and non-alcoholic beer production

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Abstract

Introduction. The aim of the present work was to substantiate for production of low and non-alcoholic beer by changing the wort composition by replacing part of the malt with unmalted barley.

Materials and methods. Industrial malt and non-malted barley were used. The alcohol fermentation was carried out using free and alginate-chitosan encapsulated top-fermenting yeast strain *Saccharomyces cerevisiae* S-33. The mashing regime included two pauses – 30 min at 50 °C and 60 min at 77 °C. The aldehydes were determined according to the bisulfite method, the ester concentration was determined by ester saponification with NaOH. Metabolites were determined after simple sample distillation of the beer.

Results and discussion. The wort extract decreased with the increase in the quantity of non-malted barley. In the selected mashing process, the fermentable sugars varied from 3.4 to 4.17% and accounted for about 50% of the laboratory wort extract. Use of 20% barley as adjunct led to a decrease in wort extract by 10% but it did not significantly affect viscosity. A major drawback of the use of non-malted barley is the increase in the laboratory wort filtration time. Filtration time was within 60–75 minutes when the adjunct was up to 20%.

It was selected to replace 20% of the malt with unmalted barley. Wort in semi-industrial conditions with the thus selected quantitative malt/barley ratio was produced (8.03% (w/w) extract and fermentable sugar content of 3.7%.). The resulting wort was subjected to alcoholic fermentation at 10 °C for 7 days with free and immobilized cells, and for each variant the fermentation kinetics were determined.

The process with free cells was relatively slow and in the first 2–3 days up to 0.4% of alcohol was accumulated, which corresponds to a fermentation rate of 11%. Changes occurred in secondary metabolism – increased ester production, normal higher alcohol formation and weak carbonyl compounds synthesis. In the immobilized cells, the fermentation start was also delayed. The actual process started after the 4th day, the fermentation quickly caught up with the free cell fermentation. As a result, more alcohol (about 0.7% w/w) was accumulated in the laboratory beer, thus enabling its classification as low-alcohol beer, and, fewer metabolites accumulated in the beer, which, in combination with the low fermentation temperature, had a negative effect on the taste profile.

Conclusions. Technological regimes for production of low alcohol and non-alcoholic beer have been selected on the basis of analysis of wort sugars, as well as on a study of fermentation kinetics at low temperatures with free and immobilized yeast cells.

Introduction

The physical methods for non-alcoholic transformation of ready-made standard beer are mainly used [1, 2]. On the one hand, this is easier to do, even at an increased cost of purchasing additional equipment. The main disadvantage of the physical removal of alcohol are the drastic changes that occur in the organoleptic profile of the final product [3].

Biological methods – changes in fermentation and mashing regimes, the use of genetically modified microorganisms or transgenic barley, in turn, make it possible to reduce the alcohol content and preserve the organoleptic profile of beer [2, 3].

Two groups of methods out of these methods are most often used – changes in the mashing mode, which ensures the production of wort with reduced content of fermentable sugars or changes in the fermentation mode – limited fermentation or stopped fermentation. Data on these methods are relatively scarce, and recent research dates back to the last decade of the 20th century, which makes them out of date [1, 3].

In the context of brewing, adjuncts are alternative sources of fermentable extract and are used to replace a portion of the barley malt, which is usually more expensive. An obvious brewing adjunct is non-malted barley. It can replace up to 50% of the malt, but it has to be ground finely, the mashes have to be thin (ratio 1:4.5), and varieties with low gelatinization temperature are preferred. With the increase in the addition of barley, the β-glucan concentration rises arithmetically, and viscosity increases exponentially [5, 6].

Immobilized cells offer the possibility of scaling up the processes in a continuous mode, which ensures the production of beer with reduced alcohol content. Although some attempts have been made worldwide, detailed studies of the possibility of applying this type of systems in beer production have not been done so far [1, 4].

As already mentioned, the development of beer with reduced alcohol content is based on changes in classical technologies, which, however, is not well studied. The lack of data on the influence of the changes in the wort composition and the changes that occur in the fermentation process on the quality of the final product raises various questions. The data cited in the literature are insufficient [1].

The aim of the present work was to substantiate the production of low alcohol and non-alcoholic beer by changing the wort composition by replacing part of the malt with unmalted barley.

Materials and methods

Raw materials

Industrial malt (Weyermann®, Germany) and non-malted barley (Bulmalts, Bulgaria) were used. The malt and barley were coarsely ground with a Corona hand mill. The alcohol fermentation was carried out using top-fermenting yeast strain *Saccharomyces cerevisiae* S-33 (Fermentis, France).

Mashing methods

In the present study, 6 experimental variants of malt/non-malted barley (Table 1) were investigated. All mashing processes were conducted in a Lochner LB-8 modified laboratory mashing apparatus equipped with a programmable controller. 50 g of grist (according Table 1) were mixed with 250 cm^3 of distilled water heated to a temperature of 45 °C. The sample temperature was raised to 50 °C and paused for 30 min. Then the temperature was increased

at a rate of 1.5 °C/1 min. After reaching a temperature of 70-72 °C, the samples were diluted with 150 cm^3 of distilled water at the same temperature. Simultaneously, the temperature was raised to 77 °C, then there was a pause for 60 min. After the set time, the samples were removed from the mashing apparatus, cooled to 20 °C and filled with distilled water to sample weight of 500 g. The samples were filtered through Macherey-Nagel MN 614 ¼ Ø 320 mm filter paper [7].

Semi-industrial wort

The wort was produced in a 20 dm^3 laboratory scale brewery (Braumeister, Germany). 4.5 kg of grist (80% malt and 20% barley) were mixed with water at a 1:5 ratio. The mashing was performed as previously described. Lautering and boiling were conducted in the same Braumeister. The boiling duration was approximately 1 h, and Nugget hop granules were added to the wort at the beginning of the process [8].

Table 1

Experimental variants

Variant	1	2	3	4	5	6
Malt, %	100	95	90	80	70	60
Barley, %	0	5	10	20	30	40

Cell immobilization

The cells were immobilized in a 3 % calcium alginate gel. After autoclaving the alginate solution for 20 minutes at 120 °C, the solution was mixed with the cell suspension to obtain a cell concentration of 10^7 cells.cm^{-3} of gel. This suspension was forced through a syringe needle by means of peristaltic pump and dropped into 2 % (w/v) $CaCl_2$ solution. The resulting beads were approximately 2 mm in diameter. The beads were left for 30 minutes in calcium solution and then number of beads were placed into 0.38 % (w/v) chitosan solution in 1% acetic acid (v/v). Alginate beads stayed in chitosan solution for 60 minutes. Afterwards, chitosan-alginate beads are washed with physiological solution (saline) to remove the excess of chitosan. Then the beads was transferred in in 0.05 M sodium citrate solution for 30 minutes for constructing microcapsules with liquid core. Afterwards, chitosan-alginate beads with liquid core were washed with physiological solution (saline) [8].

Wort fermentation

The fermentations were carried out in 500 cm^3 plastic bottles equipped with an airlock system (in order to take samples daily and to reduce the impact of the changes in the sample volume). 400 cm^3 of wort were placed into bottles and inoculated with a 10^7 cells.cm^{-3} yeast suspension. The bottles were incubated at a constant fermentation temperature of 7 °C. For the immobilized cell variants, each bottle was inoculated with 5 g of microcapsules. The results were the arithmetic mean of two parallel fermentations [8, 9].

Analytical methods and procedures

Methods of the European Brewery Convention (EBC) [10]:

- Original, apparent and real wort extract – Methods 8.3 and 9.4;
- Final, real and apparent fermentation degree – Method 9.5;
- Alcohol concentration – Method 9.2.1;
- Vicinal diketones – Method 9.24.1.

Methods for metabolite determination [11]

- Determination of the acetaldehyde content of beer – the aldehyde concentration was determined according to the bisulfite method after simple sample distillation of the beer.
- Determination of the ester content of beer – the ester concentration was determined by ester saponification with NaOH after simple sample distillation of the beer.
- Determination of the higher alcohol content of beer – the higher alcohol concentration was determined according to the Komarovsky-Felenberg method after simple sample distillation of the beer.

Biomass concentration [8]

The biomass quantity was determined by the calculation procedure based on Balling's equation.

Determination of fermentable sugars by HPLC [7]

Samples were diluted in a ratio of 1:1 with distilled water and injected directly into the apparatus under the following conditions: Apparatus – Waters 2695 (UK), Refractive index Detector 2414; Mobile Phase – 80% acetonitrile/20% water; column – Thermo ODS HYPERSIL, 250 x 4,6, flow – 1.5 ml/min; mode – isocratic [7].

The results of all standard and HPLC analysis were expressed as the mean ± the standard deviation of three replicates.

Kinetic evaluation

The kinetic evaluation was performed according to equations (1) to (5) [8].

$$\left|\begin{array}{l} \frac{dX}{d\tau} = \mu X \\ \frac{dP}{d\tau} = qX \\ \frac{dS}{d\tau} = -\frac{1}{Y_{X/S}}\frac{dX}{d\tau} - \frac{1}{Y_{P/S}}\frac{dP}{d\tau} \\ \frac{dE}{d\tau} = Y_E \mu X \\ \frac{dHA}{d\tau} = Y_{HA} \mu X \\ \frac{dA}{d\tau} = Y_A \mu X - k_A XA \\ \frac{dVDK}{d\tau} = Y_{VDK} \mu X - k_{VDK} XVDK \end{array}\right. \quad (1)$$

– Monod model with product inhibition

$$\mu = \mu_{\max} \frac{S}{K_{sx} + S + \frac{P^2}{K_{SXi}}};\ q = q_{p\max} \frac{S}{K_{sp} + S + \frac{P^2}{K_{SPi}}} \quad (2)$$

– Monod model with product and substrate inhibition

$$\mu = \mu_{\max}\left(1-\frac{P}{P_M}\right)\frac{S}{K_{sx}+S+\frac{S^2}{K_{SXi}}};\quad q = q_{p\max}\left(1-\frac{P}{P_{MP}}\right)\frac{S}{K_{sp}+S+\frac{S^2}{K_{SPi}}} \tag{3}$$

– Mass transfer equations

$$\frac{dS_{im}}{d\tau} = K_{LS}\left(S-S_{im}\right)-\left(\frac{\mu X}{Y_{X/S}}\right)-\left(\frac{qX}{Y_{P/S}}\right) \tag{4}$$

$$\frac{dP_{im}}{d\tau} = -K_{LP}\left(P_{im}-P\right)+\left(\frac{qX}{Y_{P/S}}\right) \tag{5}$$

X – biomass concentration, g/dm^3; P – ethanol concentration, g/dm^3; S – real extract, g/dm^3; $Y_{P/S}$, $Y_{X/S}$ – yield coefficients; μ – specific growth rate, h^{-1}; q – specific ethanol accumulation rate, g/(g.h); E – ester concentration, mg/dm^3; HA – higher alcohol concentration, mg/dm^3; A – aldehyde concentration, mg/dm^3; VDK – vicinal diketone concentration, mg/dm^3; Y_{HA}, Y_E, Y_A, Y_{VDK} – yield coefficients of the corresponding metabolites, mg/(g.h); k_A, k_{VDK} – reduction coefficients for aldehydes and vicinal diketones, mg/(g.h); K_{SX}, K_{SP} – Monod constants, g/dm^3; K_{SXi} , K_{SPi} – inhibition constants, g/dm^3; P_M, P_{MP} – maximal ethanol concentration for full inhibition of the process, g/dm^3; K_{LS}, K_{LP} – global mass transfer coefficients for the substrate and the ethanol, h^{-1}; P_{im} – ethanol concentration in the capsules, g/dm^3.

Results and discussion

The results for the wort extract and fermentable sugars of the six experimental variants described in "Materials and methods" are presented in Table 2. The data show that the wort extract decreased with the increase in the quantity of non-malted barley. In the selected mashing process, the fermentable sugars varied from 3.4 to 4.17% and accounted for about 50% of the laboratory wort extract. Therefore, it can be suggested that the ethanol produced during fermentation would be approximately 2% ABV.

The results in Table 2 show that up to 10% of adjunct led to the increase in the quantity of fermentable sugars. This was due to the action of the malt enzyme systems on barley starch which resulted in its hydrolysis. An increase in glucose and maltose concentration only was observed, which indicated β-amylase activity. Although the pause at 63 °C was omitted, the β-amylase action could not be ignored since it occurred but at a far from optimal rate. The over 20% increase in the non-malted barley quantity led to the accumulation of lower amounts of fermentable sugars compared to the control sample.

The data are comparable with the data cited by other authors [13, 14]. On the one hand, the data show that removing the pause at 63 °C and increasing the pause temperature for the action of α-amylase leads to a decrease in the content of fermentable extract in the wort. This, combined with the replacement of part of the malt with unmalted barley, results in a wort which is suitable for the production of beer with a reduced alcohol content.

Table 2

Composition of laboratory wort

Parameter	Malt/non-malted barley					
	100/0	**95/5**	**90/10**	**80/20**	**70/30**	**60/40**
Laboratory wort extract, % w/w	7.84 ±0.25	7.53 ±0.22	7.45 ±0.23	7.13 ±0.21	6.72 ±0.20	6.44 ±0.24
Glucose, % w/w	0.47 ±0.03	0.54 ±0.05	0.23 ±0.03	0.38 ±0.04	0.33 ±0.03	0.17 ±0.02
Fructose, % w/w	0.07 ±0.01	0.05 ±0.001	0.03 ±0.001	0.04 ±0.001	0.05 ±0.001	0.03 ±0.001
Maltose, % w/w	3.23 ±0.11	3.58 ±0.12	3.61 ±0.10	3.24 ±0.12	3.09 ±0.11	3.20 ±0.11
Fermentable extract, % w/w	3.77	4.17	3.87	3.66	3.47	3.4
Fermentable extract/wort extract, %	48.09	55.38	51.94	51.33	51.63	52.80

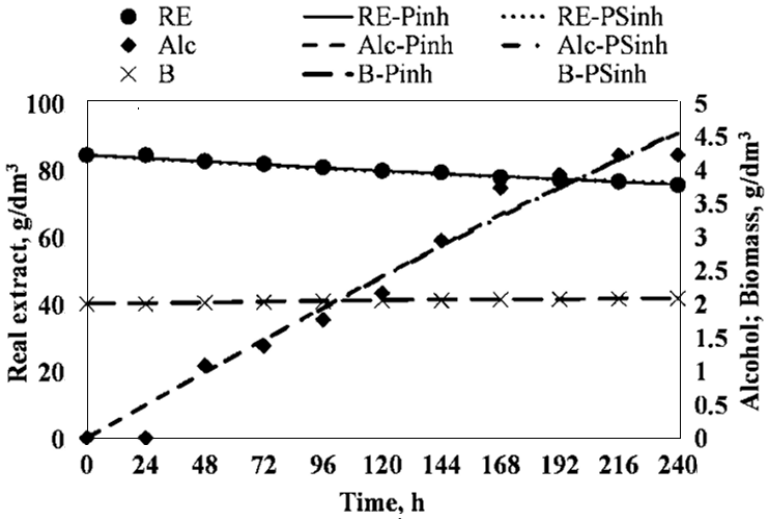
A major drawback of the use of non-malted barley is the increase in the laboratory wort filtration time. The results showed that the filtration time was within 60-75 minutes when the adjunct was up to 20%. The increase in the barley amount led to an increase in the filtration time to a value between 90 and 120 minutes because of the higher wort viscosity caused by the unhydrolyzed β-glucans. The malt enzyme system was able to hydrolyze barley β-glucan only when the adjunct was up to 20%. When the barley amount rose over 20%, an enzyme preparation with glucanase activity had to be added, which would make production more expensive [15, 16, 17].

The determination of sugar distribution into the wort can be considered a new scientific element in the development of a production technology for low alcohol and non-alcoholic beer (Table 2). The existing mashing methods that have been patented so far [18, 19] are based on empirical knowledge of the wort original extract only, which does not allow good control of the alcoholic fermentation and the accumulation of esters and higher alcohols into the beer. The maintenance of balance between fermentable sugars in the wort lies at the heart of the production of beer having a balanced profile and high quality.

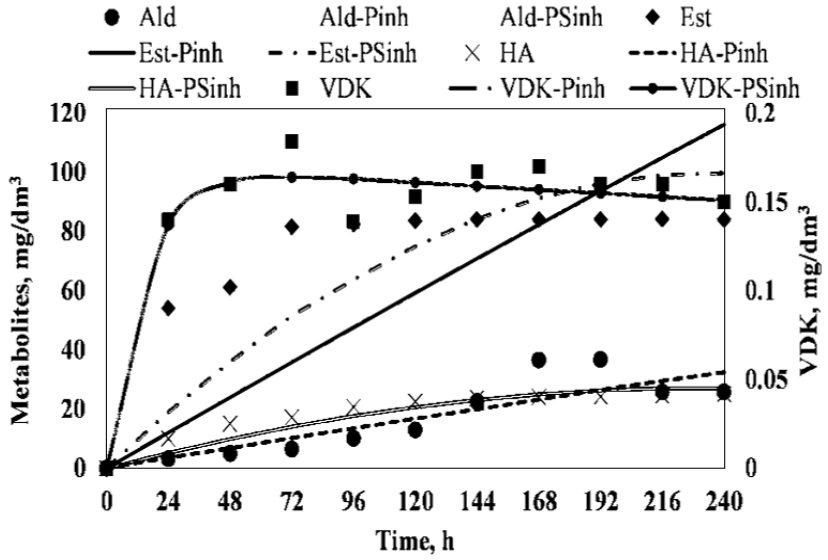
The replacement of 20% of the malt with non-malted barley was a variant selected on the basis of the data obtained for the production of low-alcohol beer.

Semi-industrial beer production with the selected variant was carried out, which included wort production in a Braumeister semi-industrial brewing system, Germany. After boiling, the resultant wort had an initial extract of 8.03 %(w/w) and fermentable sugar content of 3.7%. The wort was used for fermentation processes with free and immobilized top-fermenting yeast at 7 °C for 10 days.

The results are presented in Figure 1 and Figure 2. Identification of the parameters of kinetic models (1) to (3) was also carried out. The results are shown in Table 3, and the convergence of the models with the experimental data is presented in Figure 1 and Figure 2.



a – primary metabolism



b – secondary metabolism

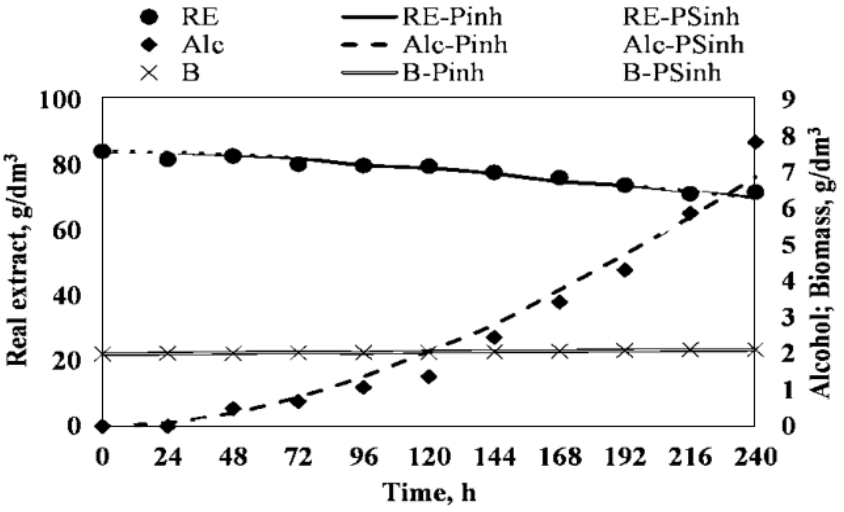
Legend:
with symbols – experimental data for fermentation parameters;
with lines – model parameters

Figure 1. Dynamics of free cell alcohol fermentation

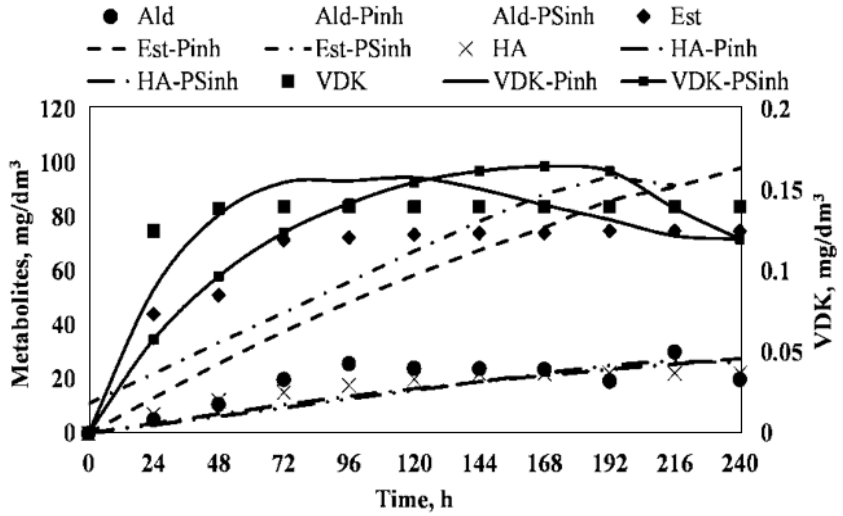
The free cell fermentation process started at a relatively slow rate. In the first 2-3 days, alcohol formation was relatively low, then culture activation began and the laboratory beer accumulated about 0.4% (w/w) of ethanol by the end of the 10th day, which gives a reason to classify the obtained beer as non-alcoholic beer. The extract consumption proceeded at a low rate and as a result, the actual fermentation rate reached 11% at the end of the fermentation. The biomass accumulation was also relatively low, which further reduced ethanol production (Figure 1a). Changes occurred in secondary metabolism. Increased ester production associated with the yeast strain used as well as with the striving of the cells to survive the stress factors was observed. The higher alcohol formation was normal. The basic amount of esters and higher alcohols were formed by the 4th – 5th day. The synthesis of carbonyl compounds was weak, and the aldehydes and the vicinal diketones in the beer were around the sensation threshold (Figure 2b). The results are comparable to those cited in [1, 20], although a more accurate comparison is difficult to make due to the strain specificity of the yeasts used. Another important feature is the differences in the analytical methods used, which also does not allow for more detailed comparisons.

In the immobilized cells, the fermentation start was also delayed. Once again, diffusion resistances affected the delay. At the low fermentation temperature, the actual process started after the 4th day, but since there was an increased volume of cells in the bottles, the fermentation quickly caught up with the free cell fermentation. As a result, more alcohol (about 0.7% w/w) was accumulated in the laboratory beer, thus enabling its classification as low-alcohol beer. The substrate uptake was also more rapid as a result of which the actual fermentation rate reached 15%. The results for the secondary metabolites were more interesting. The data reported by Naydenova, 2014 [21] that the strain used was sensitive to immobilization were confirmed. As a result, fewer metabolites accumulated in the beer, which, in combination with the low fermentation temperature, had a negative effect on the taste profile (Figure 2). However, there were no significant deviations in the taste and flavor of the beer since the high unfermented extract content concealed some of the drawbacks. The accumulation and reduction of carbonyl compounds was also delayed, which did not affect the organoleptic profile of the beer (Figure 2).

Two kinetic models reflecting different aspects of the alcoholic fermentation process were used to describe the process kinetics (Table 3). In the product inhibition model, the free cells grew at a lower specific growth rate than the immobilized cells, whereas in the product and substrate inhibition model, the reverse trend was observed due to the influence of the substrate. The first model showed that the cells demonstrated substantial lack of affinity towards the substrate (K_{SX} ranged from 3122 to 3600), which also affected the lower average specific growth rates. In the second model, there was higher affinity to the substrate, as the K_{SX} values were approximately equal to the absolute value of the substrate. The specific rate of ethanol accumulation followed a similar trend. The free cells had higher specific process rates than the immobilized cells, while the trend was reverse in the second model. Both models showed that the main substrate amount was consumed for the accumulation of ethanol. Based on the derived values for the primary metabolic model errors, the model that reflected the product and substrate inhibition showed a better match to the experimental data (Table 3). This was due to two main reasons. Firstly, it showed that the substrate had a significant effect on the fermentation process kinetics. The low concentration of fermentable sugars in combination with the low fermentation temperature resulted in greater cell dependence on the sugars. In the case of a temperature-limited fermentation process, the impact of the product inhibition was enhanced and, in combination with limited fermentable sugars, resulted in limited alcoholic fermentation. Secondly, the second model reflected the already mentioned fact that cells of the strain used were very strongly influenced by the immobilization process.



a – primary metabolism



b – secondary metabolism

Legend:
with symbols – experimental data for fermentation parameters;
with lines – model parameters

Figure 2. Dynamics of immobilized cell alcohol fermentation

Table 3

Kinetic characteristics of alcoholic fermentation

Monod model with product inhibition								
Primary metabolism	**μ_{max}**	**Ksx**	**q_{pmax}**	**Ksp**	**Yx/s**	**Yp/s**	**Ksxi**	**Kspi**
Free cells	0.0080	3600	0.0103	0.958	0.0660	0.6079	0.339	0.823
	Error=0.0038467							
Immobilized cells	0.0122	3122	4.29	97	0.0634	3.046	0.889	3.723
	Error=0.0035487							
Secondary metabolism	**Y_A**	**k_A**	**Y_E**	**Y_{HA}**	**Y_{VDK}**	**K_{VDK}**	**K_{LS}**	**K_{LP}**
Free cells	0.491	0.00115	1.38	0.383	0.0323	0.0346	-	-
	Error=2.140							
Immobilized cells	0.608	0.0044	0.909	0.256	0.0076	0.0109	0.0464	0.0016
	Error=1.354							
Efficiency coefficients	**η_μ**	**η_q**	**η_A**	**η_{KA}**	**η_E**	**η_{HA}**	**η_{VDK}**	**η_{KVDK}**
	1.386	416.50	1.238	2.933	0.658	0.668	0.235	0.315
Monod model with substrate and product inhibition								
Fermentation type	**μ_{max}**	**Ksx**	**q_{pmax}**	**Ksp**	**Yx/s**	**Yp/s**	**Ksxi**	**Kspi**
Free cells	0.132	43.48	1.549	40.78	0.0034	0.718	0.187	0.568
	Error=0.0399							
Immobilized cells	0.0323	49.92	0.497	13.52	0.0055	0.397	0.681	6.98
	Error=0.00831							
Secondary metabolism	**Y_A**	**k_A**	**Y_E**	**Y_{HA}**	**Y_{VDK}**	**K_{VDK}**	K_{LS}	K_{LP}
Free cells	0.413	0.00019	1.445	0.396	0.0061	0.0043	-	-
	Error=1.3582							
Immobilized cells	0.600	0.0046	0.878	0.249	0.0056	0.00819	0.0019	0.0012
	Error=2.140							
Efficiency coefficients	**η_μ**	**η_q**	**η_A**	**η_{KA}**	**η_E**	**η_{HA}**	**η_{VDK}**	**η_{KVDK}**
	0.245	0.321	1.453	24.21	0.604	0.629	0.918	1.904
Full inhibition	**P_{iM}**	**P_{iMP}**	$\eta = \frac{\text{Parameter for immobilized cells}}{\text{Parameter for free cells}}$					
Free cells	44.55	15.952						
Immobilized cells	64.57	475.00						

* symbols and parameters – according legend for equation (1) to (5)

The higher accuracy of the product and substrate inhibition model also reflected the higher accuracy of the parameters of the secondary metabolism. The kinetic parameters in Table 2 indicated that the immobilization process affected the secondary metabolism of cells to a certain extent, and this resulted in lower yield coefficients and reduction coefficients of the major metabolite groups in beer (except for aldehydes and the reduction of the vicinal diketones), which was also reflected in the local concentrations observed. As already commented, the results are close to those in other studies, but a qualitative comparison is difficult to make, because in addition to the specific strain, the fermentation conditions and the wort composition have an impact [1, 20].

The values of the summarized mass exchange coefficients K_{LS} and K_{LP} are of interest. In our previous studies [8, 9, 21], it was found that internal diffusional resistances have greater influence on the fermentation process than external diffusional resistances. In this regard, the K_{LS} and K_{LP} data show that they are in the same range, which means that the mass transfer in the system is more limited by the diffusion of the substrate and the product in the capsules and by the concentration difference than by the mass transfer through the stationary

layer on the surface of the capsule. The second model demonstrated that full inhibition of the cell growth occurred at relatively high ethanol concentrations (between 44.55 and 475.00 $g.dm^{-3}$), which were too far from the scope of the conducted study.

No data have been found in the specialized literature on studies of the kinetics of the fermentation process for the production of beer with reduced alcohol content. The data presented show that the study is innovative and allows the fermentation regimes studied to be transferred from laboratory and semi-industrial conditions to industrial production. In addition, the data obtained on the kinetic parameters for the accumulation of the relevant metabolites make it possible to evaluate the influence of the fermentation conditions on the organoleptic profile of the beer. As a future study, the resulting regimes will be transferred continuously to reduce beer production time to 3–4 days.

Conclusion

1. A mashing method by replacing 20% of the barley malt with unmalted barley in order to reduce the amount of fermentable sugars was proposed. As a result of the substitution, the amount of fermentable extract in the wort was 51.33%, which guaranteed the production of low alcohol and non-alcoholic beer.
2. Increasing the unmalted barley above 20% further reduces the wort extract, but worsens the conditions for lautering of the malt mash.
3. Limited fermentation with with free and immobilized cells of a top-fermenting yeast strain *Saccharomyces cerevisiae* S-33 was performed. It was found that beer with reduced ethanol content and with a relatively balanced organoleptic profile under the selected fermentation conditions was obtained. The immobilization process led to further limitation of ethanol synthesis due to the influence of diffusion resistances in the system.
4. Based on the kinetics of the fermentation process described by the product inhibition model and the product and substrate inhibition model, the effect of the low temperature and the immobilization process on the changes in the fermentation process and the production of beer with a reduced alcohol content was determined.
5. The original elements in this study are the determination of sugars in the wort and the analysis of the fermentation kinetics. A thorough analysis of these elements determines the scientific nature of the study.

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Influence of low-gluten grain crops on beer properties

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Abstract

Introduction. The prospects of using buckwheat and buckwheat malt for the production of low-gluten beer are shown.

Materials and methods. Beer wort and beer were made from crushed white buckwheat and buckwheat malt in the ratio of 85, 90, 95 percent barley malt and 15, 10, 5 percent (crushed buckwheat and buckwheat malt). To determine the content of amine nitrogen iodometric method was used, to determine the content of reducing substances the method of Wilshteter-Schudl was used, the protein content was determined by the method of Keldal, the starch content was determined by the method of Evers.

Results and discussion. Gluten is absent in such cereals as buckwheat and rice, and in other cereals the amount of gluten is: corn 80 ppm, barley 151 ppm, wheat 162 ppm. Therefore, for the preparation of low-gluten beer, crushed white buckwheat, buckwheat malt and barley malt are recommended.

The sample with the replacement of 5% barley malt on buckwheat has the highest content of reducing substances, namely 91.0 g per 100 g of extract and amine nitrogen 167.1 mg per 100 g of extract, the content of ethyl alcohol in the finished beer 3.5% by weight at mass fraction of the actual extract of 4.83% by mass.

When replacing barley malt with crushed white buckwheat, it was better to replace it with 5% barley malt. The content of reducing substances was 86.9 g per 100 g of extract, and the content of amine nitrogen was 154.9 mg per 100 g of extract. The obtained beer of this sample has the best result in terms of alcohol content of 2.9% by weight and in terms of mass fraction of real extract – 5.53% by weight.

As the amount of crushed buckwheat and buckwheat malt increases, the amount of reducing substances and amine nitrogen decreases due to the insufficient amount of hydrolytic enzymes in barley malt, under the action of which the above substances are formed. Thus, in the sample with the replacement of 5% barley malt by buckwheat, the content of reducing substances was 92 g per 100 g of extract, and the content of amine nitrogen was 168 mg per 100 g of extract. Whereas in the sample with a substitution of 15% barley malt, these figures are 82 g per 100 g of extract and 91 g per 100 g of extract, respectively.

Conclusions. The best crop for the production of low-gluten beer is crushed white buckwheat and buckwheat malt in a ratio of 95:5.

Introduction

Studies of the following cereals were made: barley, wheat, rye, corn, buckwheat in order to select grains with minimum gluten content for the production of low-gluten beer. The content of gluten in crops such as barley, wheat, corn, buckwheat is different [2].

Therefore, studies aimed at determining the minimum amount of gluten in cereals are of particular importance [16, 17]. Wheat (gliadin), rye (secaline) and barley (hordein) prolamines are toxic to the intestinal mucosa of patients with celiac disease [8, 17] due to the high content of glutamine (30%) [4] and proline (15%) [5, 6], while prolamins of rice, buckwheat, corn are not toxic due to the lower content of these amino acids [7].

Significant scientific and applied interests are the possibility of using gluten-free raw materials for the preparation of low-gluten beer [1, 3].

In study [2] it is recommended to use up to 30% of extruded buckwheat flakes for brewing wort. The use of such an amount of unmalted raw materials necessarily requires the use of a complex of hydrolytic enzymes [15], which is undesirable in the preparation of low-gluten beer. When using barley malt, this amount of extruded buckwheat flakes will not be able to saccharify the mash, so the optimal amount of buckwheat flakes remains unknown [5], which requires additional research.

Technological, physicochemical, biochemical properties of different varieties of buckwheat were studied and the choice of its optimal amount for brewing was substantiated [20]. Beer wort was prepared in an infused manner with a dry matter content of 8%, the main indicators: reducing substances and amine nitrogen decreased with increasing amount of buckwheat. It would be necessary to investigate in more detail the process of mashing and the amount of unmalted raw materials.

The use of light buckwheat malt for the production of gluten-free beverages: bread kvass, low-alcohol beverages, gluten-free beer has been studied [19]. For example, the made gluten-free beer, for the preparation of which this raw material was used, had the following physicochemical parameters: dry matter content – 11%, alcohol content by volume – 4%, active pH – 4, color – 18.5 units. EBC, amine nitrogen – 185 mg /dm3, titratable acidity – 0.9 mol/dm3 NaOH. To determine the content of reducing substances that play a significant role in the process of brewing young and finished beer additional research is needed.

For the preparation of low-gluten beer, it is advisable to use buckwheat, as it has optimal physicochemical properties, does not contain gluten and has a unique amino acid composition, which is much better than barley [10, 11].

Therefore, for the preparation of wort, and subsequently low-gluten beer as an auxiliary raw material crushed white buckwheat and buckwheat malt was selected [1, 2].

The purpose of research is to establish the effect of white buckwheat or buckwheat malt on physicochemical and organoleptic parameters for the production of low-gluten beer.

Materials and methods

Materials

Barley malt, buckwheat malt, and crushed white buckwheat were used to prepare beer wort. The mash is prepared in an insistent way [15].

Malt wort was obtained by mashing at various temperature pauses ranging from 45 °C to 78 °C, followed by filtration, boiling with and hopping, followed by clarification and cooling [12].

The finished beer wort was fermented and rambled in the classical way. The finished beer was filtered and physicochemical parameters were determined in it [15].

Pure malt wort made from light barley malt was selected as a control sample.

Methods

Determination of extractivity in grain raw materials. Extractivities in grain raw materials were performed by the congress method [12].

The essence of the method is to convert to a solution of extractive substances of malt under the action of its personal enzymes, provided that they are close to optimal, followed by separation of the solution and determine its concentration on the Anton Paar analyzer [13].

Determination of starch content in grain raw materials. Determination of starch was carried out by the Evers method. To determine the starch content, a portion of the ground raw material was dissolved at low boil with 1% hydrochloric acid solution. The resulting clear solution was polarized on a polarimeter using a tube length of 200 mm [15].

Determination of protein content in grain raw materials. Protein determination was performed by the Keldal method. The essence of the method is that the product sample is decomposed (burned) with sulfuric acid in the presence of a catalyst, and then obtained after decomposition, bound in the form of ammonium sulfate, nitrogen is determined by titration [14].

The nitrogen content (A) as a percentage of the dry matter of barley is calculated by the formula:

$$\mathrm{A} = \frac{(a-b)\cdot 0.0014\cdot 100\cdot 100}{H\cdot(100-w)},$$

where a is the amount of sulfuric acid solution taken (0.1 mol/dm3), cm3;
b – is the amount of sodium hydroxide (0.1 mol/dm3), which is spent on back titration, cm3;
w – moisture content of flour,%;
H – portion of flour, g.

Determination of moisture in grain raw materials. Determination of humidity was performed by drying to constant weight at a temperature of 130°C [12].

$$W = \frac{m_1 - m_2}{m_1 - m_0}\times 100\%$$

W – product moisture,%;
m_0 – mass of cups without sample g;
m_1 – mass of sample cups before drying, g;
m_2 – mass of the sample cups after drying, g.

Determination of physicochemical parameters of beer wort. Determination of physicochemical parameters of beer wort (mass fraction of dry matter, titratable acidity, active acidity, bitterness, color, transparency), as mentioned above, was determined using Anton Paar analyzer [13].

Determination of reducing substances in the wort. Determination of reducing substances in the wort was determined by the method of Wilshteter-Schudl, based on the oxidation of aldose by iodine [15].

Determination of amine nitrogen content in wort. The content of amine nitrogen in the wort was determined by iodometric method (according to Pop and Stevens) [12].

The method is based on the ability of amino acids to form soluble complex compounds with copper [12]. Excess copper is filtered off, acetic acid is added to the filtrate, which cleaves copper from the complex compound to form copper acetate, and then potassium iodide is added. When the latter interacts with copper acetic acid, free iodine is released, the amount of which is proportional to the amount of copper, and hence the amount of amine nitrogen [12]. Free iodine is titrated with a solution of sodium thiosulfate in the calculation [12].

Analysis of finished beer. Physicochemical parameters in the finished beer (mass fraction of visible, actual extract, ethyl alcohol, transparency, bitterness) were determined using an Anton Paar analyzer [13].

Results and discussion

Physicochemical parameters of raw materials

In samples of different cereals their fractional composition of proteins have been studied [5], the data are given in Table 1.

Table 1

Fractional composition of buckwheat proteins and some cereals (as a percentage of total protein content)

Factions	Grain products				
	Buckwheat	Barley	Wheat	Rice	Corn
Albumins	21-24	2,8-6,4	0,5-5,2	5,8-11,2	0-10,0
Globulins	42-45	7,5-18,1	0,6-12,6	4,8-9,2	4,5-6,0
Prolamines	1,1-1,2	37,2-41,6	35,6-99	4,4-14,0	29,9-55,0
Glutelins	10-12	26,6-41,9	0-28,2	63,0-70	30,0-45,0

According to the obtained results (Table 1), buckwheat and rice are classified as gluten-free cultures and are recommended for use in dietary nutrition for patients with celiac disease [3] (other names – intestinal enteropathy, gluten intolerance, gluten atoxia). This autoimmune disease, according to the World Association of Gastroenterologists, affects about one percent of the world's population [5].

Buckwheat has the best properties for brewing, beer made from buckwheat or by replacing part of the barley malt with buckwheat in taste and color is almost no different from barley.

In the Table 2 it is shown the physicochemical parameters of the studied grain raw materials.

Table 2

Physicochemical parameters of grain raw materials

Raw	Humidity,%	Extractivity, %		Starch,%		Protein,%		Duration of filtering of a congestion, min
		Air-dry substance	Dry substance	Air-dry substance	Dry substance	Air-dry substance	Dry substance	
Barley malt	3,6	74,53	77,32	62,8	65,6	10,1	11,15	30
Buckwheat malt	4,2	61,4	66,7	66,2	68,5	12,3	12,9	45
Crushed white buckwheat	12,7	67,2	69,8	70,3	72,1	13,5	14,7	45

The dry matter extract content of light barley malt exceeds the content of buckwheat malt and crushed buckwheat and is 77.32%. But the highest protein content was found in crushed buckwheat, which is 14.7%, which is 21.8% higher than the content in barley malt and 12.4% in buckwheat.

The process of filtering the wort is much faster when using barley malt, but when using buckwheat malt or white buckwheat, the filtration process is not much longer than when using barley malt. This is due to the fact that collapsed buckwheat does not have a fruit shell, which leads to a decrease in the height of the filter layer, while slowing down the filtration rate [12, 15].

Analysis of beer wort

Physicochemical parameters of pure malt wort from light barley malt (control) with partial replacement of barley malt with crushed white buckwheat are given in Table 3.

Table 3

Physicochemical parameters of malt wort with partial replacement of barley malt with crushed white buckwheat

Mash (barley malt + crushed white buckwheat)	Content of dry substance,%	pH	Titrated acidity, mol/dm³ NaOH		Content of reducing substances, g		Content of amine nitrogen, mg	
			per 100 cm^3 of wort	per 100 g of extract	per 100 cm^3 of wort	per 100 g of extract	per 100 cm^3 of wort	per 100 g of extract
Control pure malt wort	14	5,9	2,1	5,1	10,3	71,3	22,12	152,9
95% barley malt +5% crushed white buckwheat	14	6,1	4,0	9,2	12,0	86,9	22,4	154,9
90% barley malt +10% crushed white buckwheat	14	6,1	4,1	9,5	11,0	81,4	18,2	124,4
85% barley malt +15% crushed white buckwheat	14	6,1	4,2	9,7	11,7	80,8	12,6	87,1

The best results in terms of reducing substances and amine nitrogen showed a sample of wort, which was prepared from barley malt and crushed white buckwheat in a ratio of 95:5, respectively. As the content of crushed white buckwheat increases, the content of reducing substances and amine nitrogen decreases, this is due to the fact that white buckwheat lacks enzymes and therefore reducing substances and amine nitrogen cannot be extracted into solution (pure malt wort) [7]. Therefore, in the preparation of low-gluten beer, it is proposed to use wort with partial replacement of barley malt with crushed white buckwheat in the amount of 5%.

Physicochemical parameters of malt wort with partial replacement of barley malt with buckwheat malt are given in Table 4.

Table 4

Physicochemical parameters of malt wort with partial replacement of barley malt with buckwheat malt

Mash (barley malt + buckwheat malt)	Content of dry substance,%	pH	Titrated acidity, mol/dm^3 NaOH		Content of reducing substances, g		Content of amine nitrogen, mg	
			per 100 cm^3 of wort	per 100 g of extract	per 100 cm^3 of wort	per 100 g of extract	per 100 cm^3 of wort	per 100 g of extract
Control pure malt wort	14	5,9	2,1	5,1	10,3	71,3	22,1	152,9
95% barley malt +5% buckwheat malt	14	5,9	4,5	11,9	13,2	91,0	24,2	167,1
90% barley malt +10% buckwheat malt	14	6,0	4,8	11,2	12,7	87,5	19,5	139,2
85% barley malt +15% buckwheat malt	14	5,9	4,1	9,5	11,9	82,1	13,4	92,4

The best results in terms of reducing substances and amine nitrogen content showed a sample of wort, which was prepared from barley and buckwheat malt in the ratio of 95:5%, respectively. You can also see a pattern that increasing the amount of buckwheat malt decreases the amount of reducing substances and amine nitrogen, this is due to the fact that buckwheat malt has a small amount of amylolytic and proteolytic enzymes [18, 19], so biologically active substances cannot be hydrolyzed and then extracted in solution [18, 19].

But in the production of low-gluten beer, enzyme preparations are not desirable to use, as they can harm people with celiac disease [9,16].

Comparing the two types of wort (Figure 1, 2), namely the wort made from light barley malt and crushed white buckwheat and barley malt and buckwheat malt, it was concluded that for brewing wort made from barley and buckwheat malt is better. This wort has the best physicochemical parameters, and buckwheat malt has enzymatic activity [12, 15], which allows you to hydrolyze more biologically active substances. This will further prepare low-gluten beer for prophylactic purposes [12, 15] with the best Physicochemical and organoleptic characteristics.

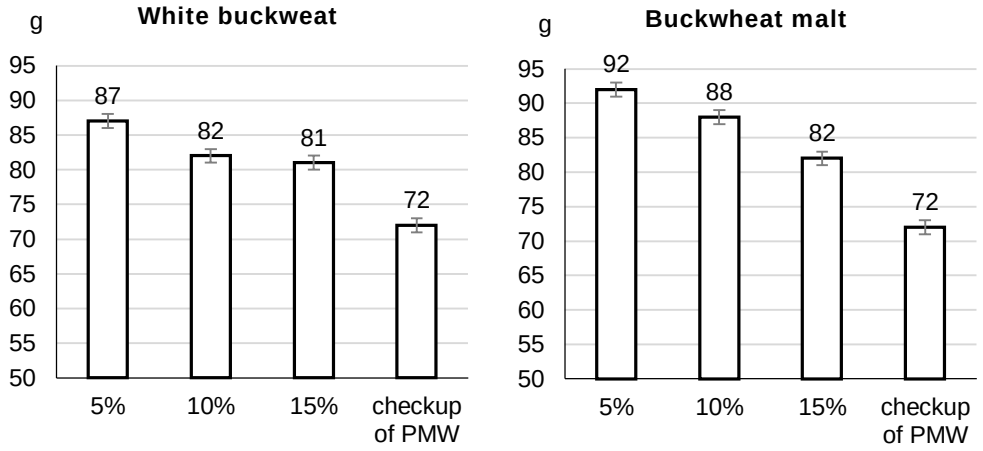

Figure 1. Content of reducing substances in malt wort from various buckwheat raw materials

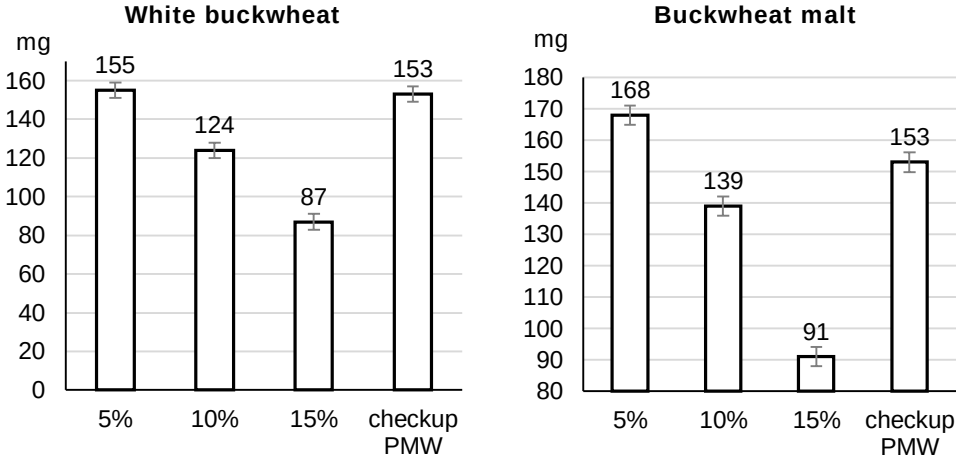

Figure 2. Content of amine nitrogen in malt wort from various buckwheat raw materials

Analysis of finished beer

The finished beer, prepared with partial replacement of barley malt with crushed white buckwheat and with partial replacement with buckwheat malt, had physicochemical parameters, which are presented in Tables 5 and 6.

As the content of crushed white buckwheat increases, the amount of alcohol changes and the mass fraction of the actual extract decreases. This is due to the fact [19] that during the main fermentation with increasing amine nitrogen, the volume fraction of alcohol increases.

Table 5

Physicochemical parameters of finished beer with partial replacement of barley malt on crushed white buckwheat

Beer samples	Content of dry substance in initial wort, %	Color, cm^3 0.1 mmol of iodine solution per 100 cm^3 of wort	pH	Titrated acidity, mol / dm^3		Content of ethyl alcohol,% wt	Mass fraction of the actual extract,% wt
				per 100 cm^3 of beer	per 100 g of extract		
Pure malt beer	14	1,55	4,3	2,3	5,7	2,8	5,51
95% barley malt + 5% crushed white buckwheat	14	1,6	4,2	2,4	5,8	2,9	5,53
90% barley malt + 10% crushed white buckwheat	14	1,7	4,3	2,5	5,9	3,1	5,46
85% barley malt + 15% crushed white buckwheat	14	1,75	4,2	2,3	5,6	3,4	5,41

Table 6

Physicochemical parameters of finished beer with partial replacement of barley malt with buckwheat malt

Beer samples	Content of dry substance in initial wort, %	Color, cm^3 0.1 mmol of iodine solution per 100 cm^3 of wort	pH	Titrated acidity, mol / dm^3 NaOH		Content of ethyl alcohol,% wt	Mass fraction of the actual extract,% wt
				per 100 cm^3 of beer	per 100 g of extract		
Pure malt beer	14	1,55	4,25	2,3	5,74	2,9	5,51
95% barley malt + 5% buckwheat malt	14	1,75	4,29	2,65	6,1	3,5	4,83
90% barley malt + 10% buckwheat malt	14	1,80	4,35	2,60	5,98	3,7	4,91
85% barley malt + 15% buckwheat malt	14	1,82	4,26	2,75	6,23	3,8	5,58

With an increase in the content of buckwheat malt increases the amount of alcohol and increases the mass fraction of the actual extract (Figure 3,4). The best results showed a sample made from 95% barley malt and 5% buckwheat malt, as it had optimal results in alcohol content and the best results in mass fraction of real extract, because the smaller the mass fraction of real extract, the better the yeast fermented the wort [12, 15].

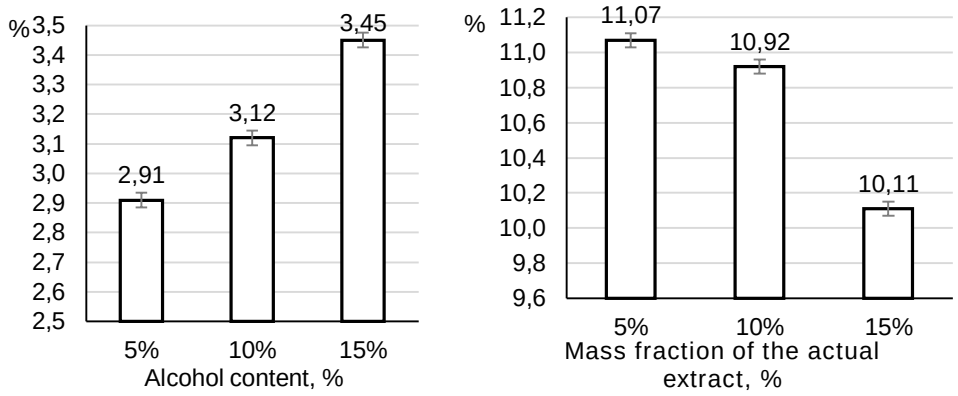

Figure 3. Effect of the amount of crushed white buckwheat on the content of ethyl alcohol and the mass fraction of the actual extract in the finished beer

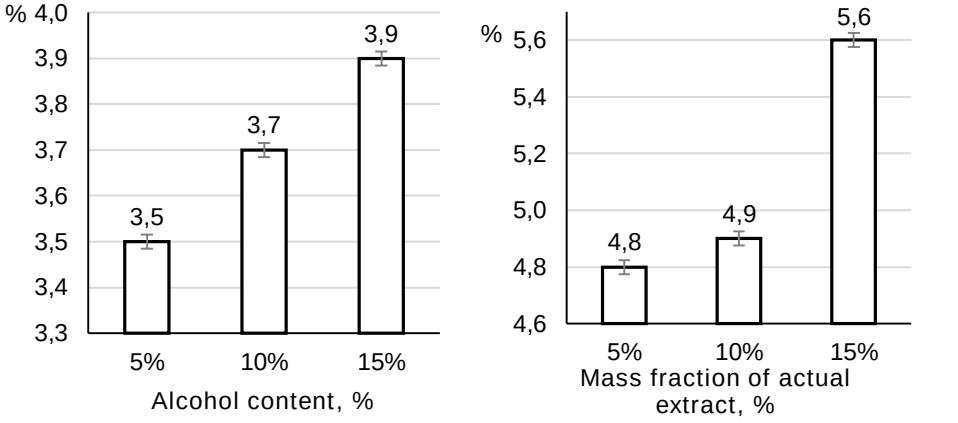

Figure 4. Effect of the amount of buckwheat malt on the content of ethyl alcohol and the mass fraction of the actual extract in the finished beer

Conclusions

The choice and quantity of unmalted raw materials – crushed white buckwheat and buckwheat malt for the production of low-gluten beer (95% barley malt and 5% buckwheat malt or crushed white buckwheat) are substantiated.

Beer brewed with a partial replacement of barley malt for buckwheat malt has better physicochemical properties than beer brewed with a partial replacement of barley malt for crushed white buckwheat.

For the production of low-gluten beer, it is recommended to use 5% buckwheat malt as a low-gluten raw material.

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Influence of physicochemical parameters of water on the amino acid composition of bread kvass

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Abstract

Introduction. The influence of drinking water, which was prepared with the help of clinoptilolite, rock crystal and activated carbon, on the amino acid composition of wort and kvass was determined.

Materials and methods. Water was prepared by treating it with clinoptilolite, activated carbon and rock crystal. The fermented wort was obtained by fermentation of rye-based wort with yeast *Saccharomyces cerevisiae* MP-10. The amino acid composition of wort and kvass was determined by ion exchange chromatography, the dynamics of kvass wort fermentation was determined by fermentation test.

Results and discussion. As a result of water treatment with clinoptilolite, activated carbon and rock crystal, the total hardness was reduced from 4.5 to 1.1 mmol/dm^3, the permanganate oxidationwas reduced from 4.0 to 0.5 mg O_2/dm^3, iron and residual chlorine were removed completely.

The change in the mineral composition of water significantly affected the course of the technological process, quantitative and qualitative amino acid composition of wort and kvass. The use of prepared water improved the qualitative amino acid composition, increased their total content in the initial wort from 3.3 to 8.87 mg/100 g, in particular amountof essential amino acids improved from 0.44 to 3.31 mg/100 g, which reduced their resynthesis, re- and deaminationby yeast cells. The total amount of amino acids in the fermented wort with using prepared water was 9.88 mg/100 g, in the control it was 5.57 mg/100 g.

The ratio of amino acids in the wort had significant differences, in particular the content of proline, which is difficult to digest by the yeast cell when using prepared water, was 14%, and for the control sample it was 30%.

Intensification of the process of yeast cells culturing increased their concentration in the culture fluid for 24 hours from 96.8 to 85.1 million/cm^3, as well as reduced the duration of fermentation of kvass wort from 15 to 13 hours.

The amino acid score of kvass,which was made withusing prepared water in the stages of yeast cultivation and fermentation of yeast wort, was more acceptable compared to the method with untreated water.

Conclusions. The use of prepared water with clinoptilolite, rock crystal and activated carbon in kvass technology improves the qualitative amino acid composition and increases their total content in the initial and fermented wort.

Introduction

The chemical composition of most soft drinks is unbalanced, which is due to the use of mainly sucrose and dietary supplements with low or no protein, dietary fiber, vitamins, minerals and other biologically active substances [1, 2].

Bread kvass, which is prepared on the basis of rye raw materials, is a traditional Slavic drink and contains a wide range of biologically active substances [3, 4].

The drink is obtained by incomplete combined alcohol and lactic acid fermentation [4, 5]. In this case, due to the activity of yeast and lactic acid bacteria, a complex of biologically active substances is formed. However, to simplify the technology, often only yeast is used, and the required acidity is achieved by adding lactic acid [3, 6, 7].

In the process of fermentation, the caloric content of the beverage decreases, the amount of digestible nutrients increases, and the biological value increases [3, 8]. However, the search for ways to increase the biological value of kvass remains relevant.

Quantitative and qualitative amino acid composition of most soft drinks is very limited [9]. Therefore, in the production of kvass it is important to preserve and accumulate in the fermentation process the maximum possible and balanced amount of amino acids, mainly essential, which determines the usefulness of the drink, affects the process and indicators of the finished product [1, 10].

It is known that the yeast *Saccharomyces cerevisiae* absorbs inorganic nitrogen, in particular ammonium sulfate, urea, ammonia salts of acetic, lactic, malic and succinic acids, as well as most amino acids [11]. However, some of the amino acids (proline, histidine, glycine, cystine) are difficult for cells to digest [12]. Therefore, it was important to conduct research to determine the effect of the amino acid composition of kvass wort on the physiological activity of yeast.

For the production of fermented beverages water from centralized water supply networks or from artesian wellsis used [13]. In the first case, the water is already reduced to drinking condition, and in the second, which is more common [3], may not meet such requirements. There are additional requirements for process water in non-alcoholic production [14], but they are absent for kvass production. In many cases, water-softened Na-cationite filters are used, but such treatment only replaces calcium and magnesium ions with sodium ions [15]. Therefore, it is important to improve the technology of water treatment with the use of effective and practically convenient natural minerals of various types during mechanical filtration.

Water treatment using mechanical filters with natural mineral backfill (quartz sand, gravel) does not fully ensure the quality of prepared water by organoleptic, physicochemical and microbiological parameters [5]. Therefore, it is important to improve the mechanical filtration of water with the use of new effective natural materials, including minerals. Due to strictly defined pore sizes and internal cavities, they are effective sorbents of organic and inorganic substances [16]. Such materials have the ability to improve the organoleptic and physicochemical parameters of water, to ensure its structuring, which increases the health effects of the finished drink [3, 13].

The use of minerals can solve various problems [4]. Sorption processes can be provided not only by the use of activated carbon and its analogues (graphite-mineral sorbents) [15]. For these purposes, as well as a filter material, it is advisable to use zeolites, in particular clinoptilolite [17].

Due to the specific structure of clinoptilolite, which is a tetrahedron with octagonal rings on the tops containing alkaline and alkaline earth metals inside the cations and a significant

number of entrance windows (3.5–4.8 A^0) and channels, its use as a molecular sieve with ion exchange properties is ensured [15].

The aim of the work is to study the effect of clinoptilolite, rock crystal and activated carbon in the preparation of water on the amino acid content in the original and fermented wort to improve the viability of yeast and obtain the finished drink with balanced amino acid composition.

Materials and methods

Water treatment using clinoptilolite, activated carbon and rock crystal

Tap water treatment was performed with clinoptilolite of Sokyrnytsia deposit (Ukraine), activated carbon and rock crystal at a speed of 8–15 m/h. Water was prepared in a cyclic mode with the following sequential operations:

- Preparation of materials;
- Water filtration to reach the limit values: clinoptilolite for hardness; rock crystal for transparency; activated carbon for transparency, color and permanganate oxidation;
- Padding of a layer of materials with a stream of untreated water for prevention of caking and removal of dirt from their surface;
- Regeneration of clinoptilolite.

The use of clinopylolite is due to the fact that it reduces the hardness of water and removes heavy metals [17].

Activated carbon was used to reduce the content of organic impurities and improve the organoleptic characteristics of water [3].

Rock crystal was used to structure the water, adjust the redox potential and remove foreign microflora [15].

In the prepared water the content of total iron was 0.01 mg/dm^3, total hardness 1.1 mmol/dm^3, permanganate oxidation 0,5 mg O_2/dm^3. Untreated water with a total iron content of 0.05 mg/dm^3, a total hardness of 4.5 mmol/dm^3, and a permanganate oxidation of 4.0 mg O_2/dm^3 was used as a control.

Preparation of kvass wort and kvass

For the cultivation of yeast, wort was prepared from a concentrate of kvass wort, sugar syrup and water with concentration of 7.0–8.0% of dry matter [13]. The wort for kvass preparation was prepared to a dry matter concentration of 3.4–3.6%, it was fermented with a pure culture of yeast *Saccharomyces cerevisiae* MP-10, which was selected from acidic concentrate of kvass wort (patent № 134310 Yeast strain *Saccharomyces cerevisiae* MP-10 using for fermentation in the production of fermented beverages) with the initial yeast cells concentration of 0,6 million/cm^3 at a temperature of 34 °C to reduce the dry matter content by 0.8–1.0%. The fermented wort released from the yeast sludge was blended to a dry matter content of 5.4–5.6% [4].

Two samples of kvass wort were prepared:

- Control – wort with untreated water;
- Experiment – wort with prepared water.

Determination of yeast fermentation activity

The concentration of yeast cells in the culture fluid was determined using the Goryaev chamber [18], the dynamics of fermentation of yeast wort was determined by biological method.

Determination of amino acid content

The amino acid composition of wort and kvass was determined by ion exchange chromatography on Biotronik Amino Acid Analyzer LC2000 equipment with amino acid distribution using ion exchange resin and tribuffer system. Identification was performed by reaction with ninhydrin and detection with photocolorimetery and electrophoresis methods using the system «Drops-105/105M», which involves acid hydrolysis with the transition of amino acids into free forms with their subsequent separation and quantification by capillary electrophoresis. Detection was performed in the UV region of the spectrum at a wavelength of 254 nm [4].

Determination of amino acid score

To characterize the biological value of kvass, we compared their amino acid composition with the ideal scale of amino acids [19, 20]. Amino acid score was calculated by the formula:

$$C = (A / H) \cdot 100,$$

where:

C is score,%;

A is amino acid content in kvass, mg/g protein;

H is the amino acid content in an ideal protein, mg/g protein.

Results and discussion

Influence of filter materials on physicochemical parameters of water

Water used for the production of fermented beverages must be epidemiologically safe, harmless in chemical composition and have acceptable organoleptic properties [13, 21].

Physicochemical parameters of control and experimental water samples are given in Table 1.

It is established that the joint use of the studied rawmaterials provided the necessary physicochemical parameters of process water. The total hardness was reduced by 82%, the permanganate oxidation was reduced by 3.6 times, iron and residual chlorine were removed completely.

In the first stage, the water was treated with clinoptilolite to reduce stiffness and remove mechanical impurities [15]. This reduces the load on the carbon filter, which increases its service life [4]. Treatment of water with activated carbon in the second stage provided sorption of impurities, stabilization of the redox potential and improvement of organoleptic characteristics [3]. The third stage involves the treatment of water with rock crystal for its structuring and design of organoleptic characteristics [13].

Table 1

Influence of filter materials on physicochemical parameters of water

Sample name	Dry residue, mg/dm^3	Total stiffness, mmol/dm^3	Total iron, mg/dm^3
Control	251.0	4.5	0.05
Experiment	205	1.1	less than 0.01

Sample name	Cl^-, mg/dm^3	NO_3^-, mg/dm^3	SO_4^{2-}, mg/dm^3	pH	Permanganate oxidation, mg O_2/dm^3
Control	34	4.6	37	7.39	4.0
Experiment	15	less than 0.05	15	8.10	0.5

Effect of water on the amino acid composition of the original kwass wort

The main amine nutrition for yeast in kvass wort is free amino acids [22], which directly affect their physiological activity [23, 24]. Table 2 shows the amino acid content in the studied samples of kvass wort.

Table 2

Amino acid composition of kvass wort

Amino acids	The content of amino acids in the wort, mg / 100 g	
	Control	Experiment
Aspartic acid	1.65	2.85
Threonine	0	0.42
Serine	0.16	0.39
Glutamic acid	0	0.05
Proline	0.97	1.25
Glycine	0	0.05
Alanine	0	0.74
Valine	0.05	0.34
Methionine	0	0.06
Isoleucine	0.02	0.33
Leucine	0.04	0.45
Tyrosine	0	0.29
Phenylalanine	0	0.94
Histidine	0.33	0.45
Arginine	0	0
Lysine	0	0.03
Essential	0.44	3.31
Non-essential	2.86	5.56
Total	3.30	8.87

The obtained data indicate the presence of seventeen amino acids in the kvass wort, in particular 9 essential ones. When using the prepared water, the total amino acid content in the kvass wort was higher by 63%, in particular essential ones by 87%. The content of inorganic nitrogen (ammonium salt) in the test sample increased almost threefold (from 0,08 to 0,23 mg/100 g). The significant difference in the content of amino acids in the studied samples can be explained by the mineral composition of the untreated water, in particular the increased amount of hardness salts, which while interacting with organic acids change the acidity of the wort.

Amino acids in solutions exhibit the properties of amphoteric electrolytes. Depending on the pH of the medium, they can have acidic or alkaline properties. In an acidic environment, the dissociation of the carboxyl group is inhibited, the amino acid molecule thus acquires a positive charge and reacts as a cation:

$$\begin{array}{l} R - CH - COO^- + H^+ \rightarrow R - CH - COOH \\ \quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad | \\ \quad NH_3^+ \quad\quad\quad\quad\quad\quad\quad NH_3^+ \end{array}$$

In an alkaline environment, under the action of OH- ions, the ionization of amino groups is inhibited, the amino acid molecule acquires a negative charge and reacts as an anion:

$$\begin{array}{l} R - CH - COO^- + OH^- \rightarrow R - CH - COO^- + H_2O \\ \quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad | \\ \quad NH_3^+ \quad\quad\quad\quad\quad\quad\quad NH_2 \end{array}$$

The pH value of the medium at which the total charge of the amino acid is zero is called the isoelectric point [25–27]. Therefore, the pH of the wort has a significant effect on the process. Table 3 shows the acidity of the kvass wort of the test samples.

Table 3

Acidity of kwass wort

Sample name	Titrated acidity, cm^3 of NaOH solution conc. 1 mmol/dm^3 per 100 cm^3 of wort	pH
Control	0.9	5.94
Experiment	1.2	5,45

It is known that the isoelectric point for monoaminomonocarboxylic acids corresponds to pH 6. In isoelectric points of amino acids are the least stable and precipitate directly and in the form of salts. According to the data, the active acidity of the wort of the control sample in contrast to the experimental was close to this value.Therefore, the content of monoaminomonocarboxylic acids in the test sample was 2.78 mg/100 g, which is 10 times higher than in the control (see Table 2).

Yeast assimilates amino acids in different sequences [26]. Table 4 shows the distribution of amino acids by their digestibility.

Table 4

Distribution of amino acids by digestibility by yeast species *Saccharomices cerevisiae*

Class 1	Class 2	Class 3	Class 4
Arginine	Histidine	Alanine	Proline
Aspartic acid	Isoleucine	Glycine	-
Glutamic acid	Leucine	Phenylalanine	-
Lysine	Methionine	Tryptophan	-
Serine	Valine	Tyrosine	-
Threonine	-	-	-

Figures 1 and 2 show the ratio of the above classes of amino acids in the studied samples of wort.

These data indicate that the test sample contained a larger range of amino acids compared to the control, which promotes their assimilation by yeast in the first stage of reproduction with little resynthesis, re- and deamination [26]. In this case, amino acids are used by cells for protein synthesis directly, and therefore their assimilation is more efficient [4]. The content of proline, which is difficult to digest by the yeast cell was 2 times less than in the control. It should also be noted that the test sample, in contrast to the control, contained methionine, which is a partial source of phosphorus nutrition for yeast [19].

The assimilation of amino acids by yeast occurs in two ways, one of which is associated with deamination and the other with decarboxylation [27, 28]. Decarboxylation occurs according to the equation:

$$RCHNH_2COOH \xrightarrow[\text{proteid}]{\text{pyrodoxal}} RCH_2NH_2 + CO_2$$

The deamination reaction is associated with the release of ammonia from the amino acid by the equation:

$$RCHNH_2COOH + \frac{1}{2}O_2 \rightarrow RCOCOOH + NH_3$$

The deamination process is associated with reamination reactions. These two processes allow cells to synthesize amino acids most intensively [29].

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

Qualitative and quantitative composition of amino acids of wort determines the biosynthetic processes of yeast cells and directly affects the rate of their growth [3, 13]. Tables 5, 6 show a comparative characteristic of the concentration of yeast cells and their specific growth rate during cultivation.

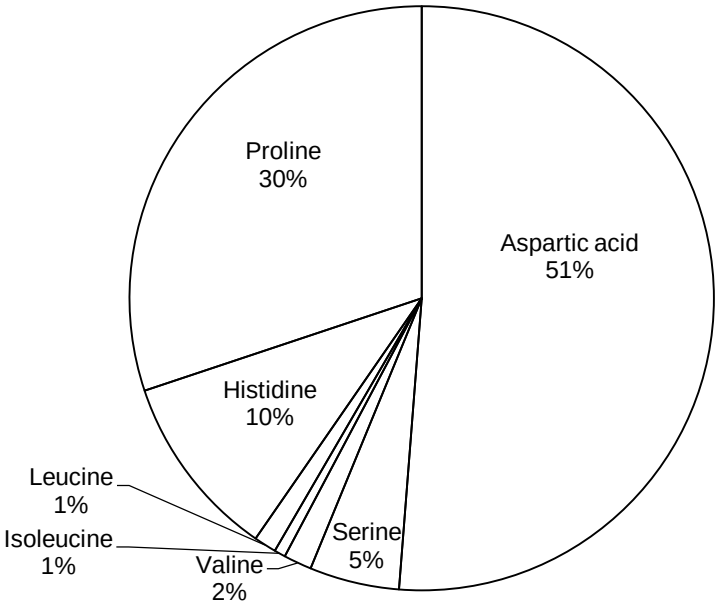

Figure 1. The ratio of amino acids in the wort when using untreated water (control)

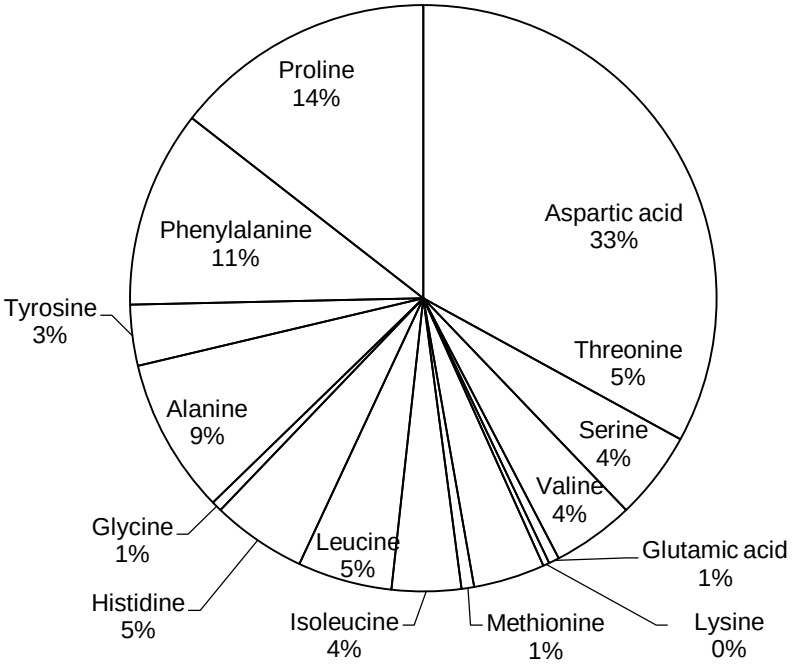

Figure 2. The ratio of amino acids in the wort when using prepared water (experiment)

Table 5

Influence of cultivation duration on yeast cell accumulation

Duration, hours	Yeast cell concentration, mln/cm^3	
	Control	Experiment
0	0.5	0.5
6	3.7	8.1
12	54.1	61.5
18	78.2	89.0
24	85.1	96.8

Throughout the cultivation process, the content of yeast cells in the test sample was higher than in the control: after 6 hours – 54%, the next – an average of 12%, which can be explained by the increased content of amino acids in the wort used as a source of amine nutrition for yeast. These data indicate a positive effect of a more balanced nitrogen nutrition of the experimental sample of yeast wort on the accumulation of yeast cells.

Table 6

Effect of cultivation duration on the specific growth rate of yeast

Duration, hours	Specific growth rate (μ), h^{-1}	
	Control	Control
6	0.333	0.464
12	0.447	0.337
18	0.061	0.062
24	0.014	0.014

When comparing the studied samples, it was found that the maximum specific growth rate of the experimental sample was 3,6% higher for the experimental sample compared to the control. Achieving high growth rate by the sixth hour of growth for this sample (28% more than in the control) indicates a reduction in the lag phase and accelerating the beginning of the phase of exponential development of yeast [9]. Subsequently, the specific growth rate of yeast in the experimental and control samples did not differ. The obtained results can be explained by the expanded qualitative composition of amino acids in the experimental sample, which are not close to the isoelectric point and do not precipitate. After 18 hours in the culture medium there was a phase of cell death, which was accompanied by a decrease in the specific growth rate.

Figure 3 shows the dynamics of the decrease in dry matter content during the fermentation of wort by yeast at the initial cells content in the inoculumof 61 million/cm^3 in the phase of their exponential growth.

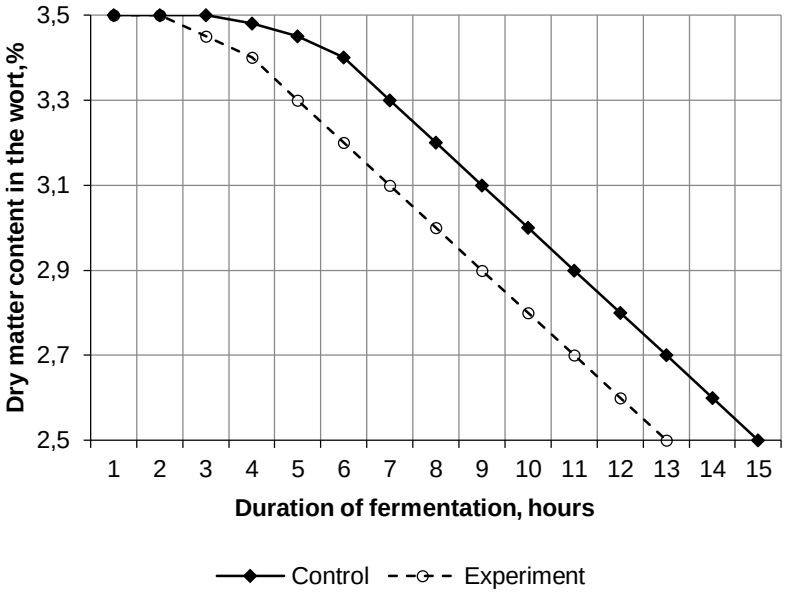

Figure 3. Dynamics of dry matter content during fermentation of kvass wort

The general nature of the fermentation process in the studied samples was similar. However, in the experimental sample the beginning of intensive fermentation was observed from the second hour, and in the control – from the third, which can be explained by more active physiological state of yeast, reducing the duration of their adaptation to environmental conditions [26], increased initial amine nitrogen content. In addition, calcium, magnesium, and sodium ions, which reduce the permeability of the yeast membrane, had a negative effect on the control sample [29]. The required decrease in dry matter content (by 0.8–1.0%) for the test sample occurred on average by 2 hours faster than control.

Effect of water on the amino acid composition of fermented kvass wort

It was found that the treated water allowed not only to preserve most of the amino acids of the kvass wort concentrate, but also to optimize their quality ratio (see Table 2). At the same time, full nutrition of yeast was provided and fermentation was accelerated, the influence of resynthesis, re- and deamination processes was significantly reduced (Figures 1, 2). It should be kept in mind that amino acids are the component not only of cell organelles, but also of enzymes and vitamins [26]. Alanine is part of pantothenic acid, which plays an important role in the life of yeast [9]. Glutamic acid is involved in the construction of enzymes that catalyze the synthesis of purine bases and peptides [19]. In addition, the qualitative composition of amino acids used for protein synthesis directly affects the stability of RNA [28, 29].

Figures 4 and 5 show the comparative characteristics of the amino acid composition of the original and fermented wort using the yeast *Saccharomyces cerevisiae* MP-10.

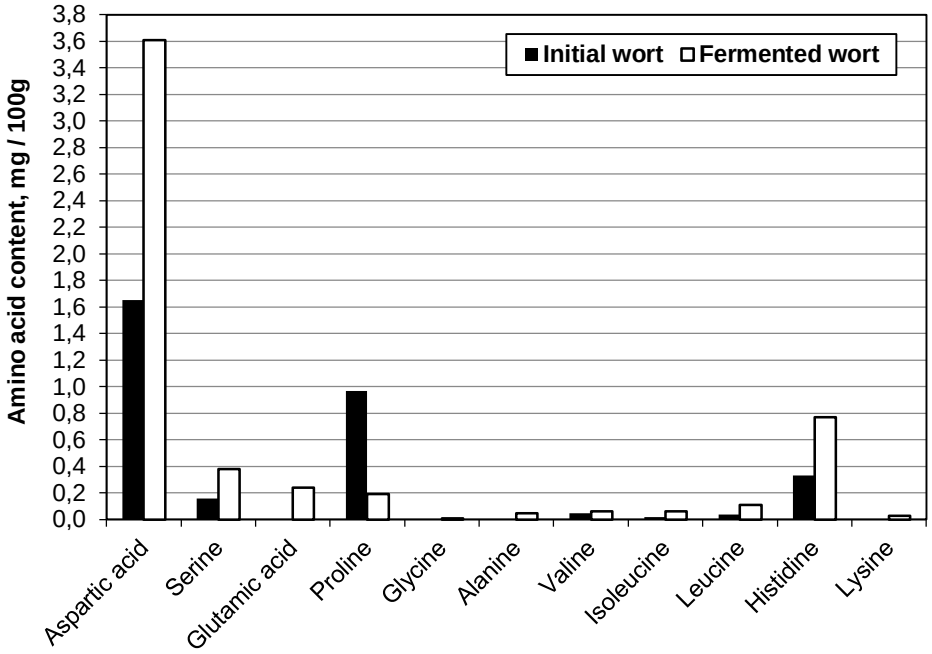

Figure 4. Amino acid composition of the wort when using untreated water (control)

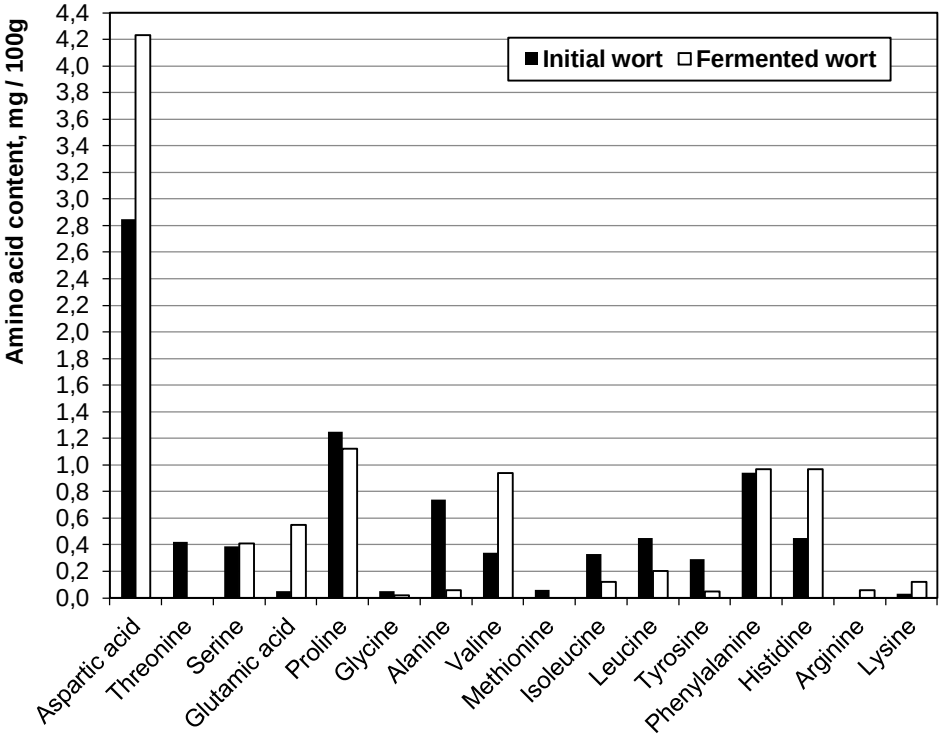

Figure 5. Amino acid composition of the wort when using prepared water (experiment)

During fermentation, the content of amino acids changed significantly at their relatively constant ratio – 40 and 10% for experimental and control samples, respectively. The total amount of amino acids in the experimental sample of fermented wort was 9,88 mg/100 g, in the control 5.57 mg/100 g, respectively .

The possibility of protein utilization by the human body is due to the minimum score of one of the essential amino acids [14]. The main one is not the quantitative content of biologically active substances, but their adequacy in accordance with the needs of the human body [2, 7, 19]. Therefore, to characterize the biological value of kvass obtained from the studied samples, we compared their amino acid composition with the ideal scale of amino acids. The amino acid score of the kvass samples is shown in table 7.

Table 7

Amino acid score of kvass

	Amino acid					
Sample	**Valine**	**Histidine**	**Isoleucine**	**Leucine**	**Lysine**	**Phenylalanine + tyrosine**
Control	12	334	15	16	5	0
Experiment	188	421	30	29	22	170

In the studied kvass samples, the amino acid score did not meet the requirements of an ideal protein, which is typical for most foods [4, 7, 20]. However, the amino acid score of experimental sample was closer to the ideal protein than the test sample (leucine, isoleucine and lysine). Lysine was determined as the limiting amino acid for both samples. Phenylalanine and tyrosine were absent in the control sample.

Therefore, kvass prepared using clinoptilolite, activated carbon and rock crystal in water treatment had increased biological value.

Conclusions

1. The use of prepared water improves the qualitative amino acid composition, increases their total content in the initial wort by 63%, including essential by 87%, which reduces their resynthesis, re- and deamination by the yeast cell. The content of monoaminomonocoarboxylic acids in the test sample in comparison with the control increases by 10 times.
2. Water treatment with clinoptilolite, activated carbon and rock crystal intensifies the process of yeast cultivation and increases its concentration in the culture fluid by 12%. During the fermentation of kvass wort, the normative decrease in the dry matter content for the experimental sample occurred on average 2 hours faster compared to the control.
3. The amino acid score of kvass which was made by using prepared water is more acceptable compared to the use of untreated water. Prepared water provides an increase in the quantity and improvement of the qualitative amino acid composition of bread kvass.

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Effect of chufa flour addition on characteristics of yoghurt quality

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Abstract

Introduction. The purpose of the research is to determine the effect of the addition of chufa flour on the characteristics of yoghurt quality.

Materials and methods. The yoghurt has been prepared by respecting the classic technological process, with the difference that chufa (*Cyperus esculentus*) flour has been added in different proportions (sample ICO3–0.3%, ICO5–0.5%, ICO7–0.7%). The yoghurt samples have been kept at a temperature of 2–4 °C for 15 days. Diacetyl has been determined by gas chromatography method, titratable acidity of yoghurt samples – by titration with 0.1N NaOH and syneresis – using the methodology of Barkallah.

Results and discussion. After the first day of storage, the diacetyl content is low in all the analyzed samples, but the ICO5 sample showed a higher diacetyl content of 6.5 μg/g. After 15 days of storage, the diacetyl content increased in all samples analyzed, so so diacetyl content of control sample is 6.4 μg/g, ICO3 – 15 μg/g, ICO5 – 16.2 μg/g and ICO7 18.8 mg/g. The high content of diacetyl is found in ICO7, which means that the addition of chufa flour has a positive effect for lactic acid bacteria used in the fermentation process. The acidity increases in all yoghurt samples analyzed from day 1 to day 15. The control sample shows lower acidity values between 80 and 108 °T, compared to the other samples, but the sample with a chufa flour in the proportion of 0.7% has acidity values between 87 and 125 °T, which indicates that the addition influences this characteristic analyzed. The highest removal of the serum was observed for control sampkle in 1 and 15 days, compared to the samples ICO3, ICO5 and ICO7. The ICO7 sample shows a lower syneresis, respectively on the first day of 9%, and the on 15th day of 32%.

Conclusions. The addition of chufa flour improves the quality of yoghurt, which is of particular importance to the consumer in choosing these dairy products.

1. Introduction

Consumption of yoghurt has several benefits for human health, such as protection against gastrointestinal upsets, enhanced digestion of lactose by maldigestion, decreased risk of cancer, lower blood cholesterol, improved immune response and help the body assimilate protein and calcium [2–4]. The demand for dairy products with functional properties leads to the promotion of added-value products: fermented dairy drinks, probiotic and other functional yoghurts, reduced-fat and enriched milk products and other [26]. Another important trend is the increasing demand for consumer convenience. Consumers prefer foods that promote good health and prevent diseases [27].

Many researchers have conducted studies on improving the composition of yoghurt by using it with milk proteins or vegetable proteins [5–8]. One of the ways to improve the nutritional value of yoghurt is to use the chufa (*Cyperus esculentus*). The chufa has been shown to have various beneficial health effects such as preventing obesity and lowering cholesterol and triglycerides. [9, 28] Its chemical composition includes fibre, protein and natural sugars. Moreover, chufa has a high content of soluble glucose and oleic acid, along with high energy content (starch, fats, sugars and proteins), are rich minerals such as phosphorous, potassium and in vitamins E and C [10]. The chufa flour can also be considered an excellent source of natural antioxidants (mainly flavonoids) and a natural food additive [11]. These numerous nutritional advantages and health benefits associated with chufa makes it more attractive for dairy products.

The sample of application of chufa flour in food technology is the production of "Horchata de chufa" ("tiger nut" or "chufa" milk), is a sweetened water extract of chufa tubers, which is popular in Spain [29]. Adgidzi et al. [30] investigated yoghurt-like products from chufa. The use of chufa and cow milk composite to prepare yoghurt reduces the cost of yoghurt production without compromising its nutritional composition and therapeutic effects. It is possible to manufacture probiotic yoghurt using chufa extract as a functional dairy food [31]. A product known as cypher-coconut yoghurt can be prepared using coconut milk blended with chufa milk, and the commercially available starter used as a source of lactic acid bacteria [32]. It is also used as a flavouring agent in ice cream [33]. Ice cream production from a blend of chufa and cow milk was subjected to proximate, physicochemical and sensory evaluation by Umelo et al [33]. Flour of roasted chufa is sometimes added to bakery products [34], as well as in making oil, starch extracts and soap [35].

However, it's not enough nutritional advantages and health benefits of the product for successful commercial promotion, and it's necessary to supply good sensory properties of new a product. Generally lactic acid gives fermented milk their slightly tart taste. Other typical flavours and aromas are additional results of LAB metabolism [36]. Thus, more than 100 chemical compounds was isolated from yoghurt and other fermented milk, but only a few (ethanol, diacetyl, acetaldehyde, acetone and butanone-2) influence on the desired product flavour [37, 38, 39].

Acetaldehyde provides the typical aroma of yoghurt [25]. The Streptococcus may form acetaldehyde from lactose via pyruvate, but only trace amounts are formed by this way and by *Lactobacillus delbrueckii subsp. bulgaricus*. Optimum aroma and flavour are obtained between 23 and 41 ppm acetaldehyde. Diacetyl and acetoin result from the metabolic activity of *Streptococcus thermophilus* are very low – 0.5 ppm. Diacetyl is produced by *Lactococcus lactis subsp. lactis biovar. diacetylactis* and *Lactococcus lactis subsp. cremoris*. The presence of diacetyl contributes to the delicate, full flavour and aroma of yoghurt and is especially important, if acetaldehyde is low because it can enhance yoghurt flavour [25].

Note, in the available scientific literature there are insufficient data about the effect of the addition of chufa flour on the characteristics of yoghurt quality.

Therefore, the purpose of the research is to determine the effect of the addition of chufa flour on the characteristics of yoghurt quality. Also, an important task is to study the degree of syneresis in the product to ensure uniform consistency during storage.

2. Materials and methods

2.1. Materials and sample preparation

For yoghurt preparation, cow milk has been used. Used milk has a fat content of 1.5% because it takes into account the consumer's preference to consume dairy products with low-fat content [12, 13].

The technological scheme is identical to the classic one concerning the technological parameters [14]. For inoculation, a specific culture for the processing of yoghurt from CHR HANSEN has been used in the proportion of 0.075 g/L milk [15].

Different percentage of chufa (*Cyperus esculentus*) flour has been added before homogenization, in the following proportions: 0.3%, 0.5% and 0.7%, and the mixture obtained has been packed in glass jars with lids, placed under thermostat at a temperature of 42 °C for 3.5 hours and cooled to 20 °C for one hour. Yoghurt has been stored at a refrigeration temperature of 2–4 °C [16].

The yoghurt samples have been analyzed after two storage periods 1 day **(T1)** and 15 days **(T15)** at 4 °C.

The analyzed samples were marked as follows:

1.Control sample, yogurt with 1.5% fat: **IM**;

2.Yoghurt with a chufa flour addition of 0.3%: **IC03**;

3.Yoghurt with a chufa flour addition of 0.5%: **IC05**;

4.Yoghurt with a chufa flour addition of 0.7%: **IC07**.

2.2. Methods of analysis

2.2.1. Preparation of samples for GLC analysis

Diacetyl extraction has been performed using high purity acetone. Approximately 2 g of the sample has been accurately weighed, 2 mL of acetone and 2 mL of 2,3-pentandione of 50 μg/mL were added as internal standard and stirred vigorously for 30 seconds. After the samples were centrifuged at 4000 rpm for 5 minutes, the supernatant has been filtered through a 0.20 μm disposable syringe membrane filter and then injected directly into the gas chromatography apparatus. The final diacetyl concentration (expressed as μg of diacetyl per gram of sample) has been calculated using the following formula [11]:

$$\text{Diacetyl } (\mu g/g) = \frac{wIS \cdot AD \cdot P \cdot 0{,}5}{AIS \cdot Ws \cdot 25}$$

where:

w_{IS} – internal standard (2.3 pentanedione), µg;
A_D – diacetyl peak area;
A_{IS} – the peak area of the internal standard;
W_s – sample table, g;
P – purity of the standard, %;
0,5 – dilution factor;
25 – dilution factor.

2.2.2. Gas-chromatographic analysis

Diacetyl gas chromatographic analysis has been performed by manual injection using an Agilent Technologies Model 7890A gas chromatograph equipped with a flame ionization detector. A sequence has been created using Chem Station software to analyze the samples and quantify the results.

A 30 m YB WAX capillary column (Phenomenex, Torrance, CA.USA) with a diameter of 0.32 mm, a particle size of 0.5 µm and a composition of 100% polyethylene glycol has been used. The following parameters have been used for the analysis:

- Carrier gas, a combination of nitrogen and hydrogen at a flow rate of 50 kPa (7.25 psi);
- Injection volume: 1µl;
- Injection ratio at injection, 1:15;
- Injector temperature: 250 °C;
- Detector temperature: 260 °C;
- The oven temperature increases progressively by 7 °C/min from 50 °C to 240 °C.

The diacetyl peak recognition has been performed by comparing its retention time with that of the relative standard. The quantitative measurement of diacetyl has been calculated from the diacetyl peak area compared with that of the 2,3-pentanedione. Some samples of the gas chromatography profiles for yoghurts enriched with chufa are presented in Figures 1 and 2:

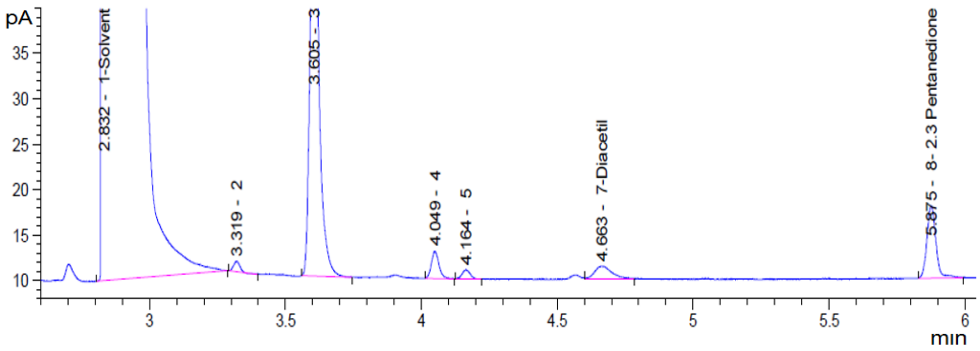

Figure 1. GC chromatogram of yoghurt with 0.3% chufa **(T1): 1-Solvent; 2, 3, 4, 5-Solvent impurities; 6-Yoghurt component; 7-Diacetyl; 8-Internal standard 2.3 Pentanedione**

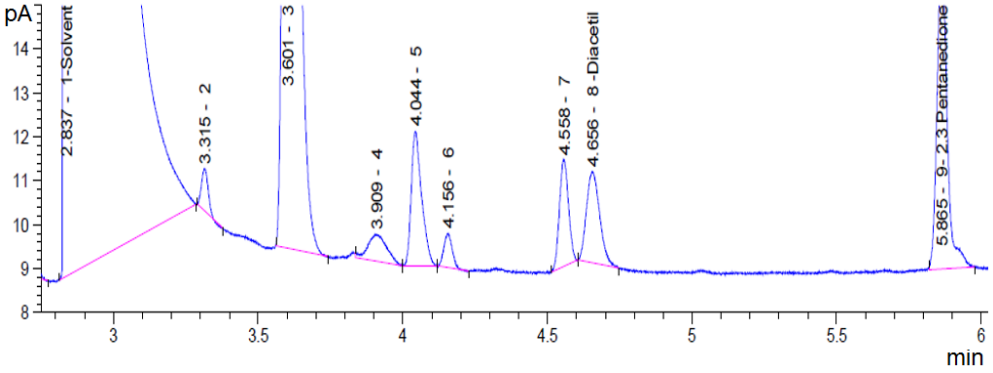

Figure 2. Gc Chromatogram of Yoghurt with chufa **0.7% (T15): 1-Solvent; 2,3,5,6-Solvent impurities; 4,7-Yoghurt components; 8-Diacetyl; 9-Internal standard 2.3 Pentanedione**

2.2.3. Titrable Acidity

Titrable acidity of yoghurt samples has been determined by titration with NaOH 0.1N solution using phenolphthalein as an indicator and expressed in Thörner degrees [20].

2.2.4. Susceptibility to Syneresis

Syneresis of the different yoghurt samples has been determined according to the methodology proposed by Barkallah et al [21] by placing 100 mL of each sample in a funnel lined with Whatman filter paper number 1. After 6 h of drainage, the volume of whey has been measured and the following formula has been used to calculate susceptibility of syneresis:

$$Syneresis = \frac{V_1}{V_2} \cdot 100$$

where,

V_1 = volume of whey collected after draining, ml;

V_2 = the volume of the yoghurt sample, ml;

3. Results and discussions

3.1. Determination of diacetyl

Figure 3 shows the results obtained for the determination of diacetyl of the samples obtained during the analyzed period.

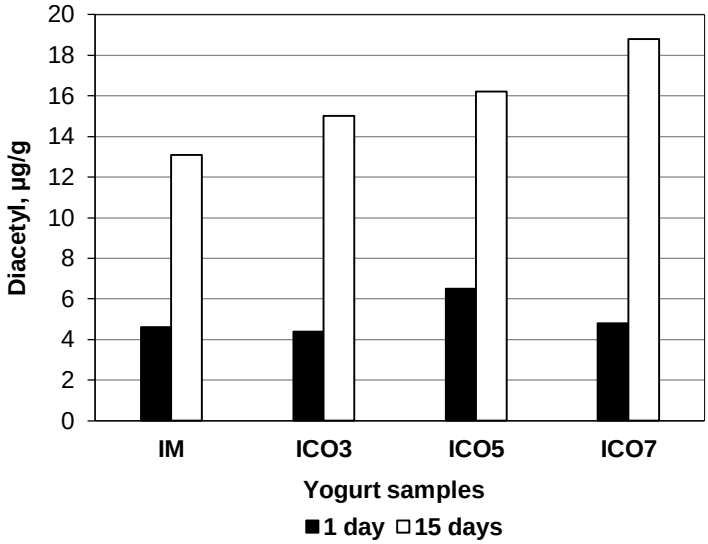

Figure 3. Evolution of diacetyl content in yoghurt samples

The diacetyl content analyzed in 1 day shows different values, so the control sample, the sample with an addition of 0.3 and the sample with 0.7% chufa between 4.4 and 4.8 µg/g, and the sample with a chufa of 0.5 has a content higher than 6.5 µg/g.

After 15 days of storage, the diacetyl content of the samples increased considerably, so the control sample has a value of 13.1 µg/g, and the sample with 0.7% chufa has the highest diacetyl content of 18.8 µg/g compared to the samples by 0.3% (15 µg /g) and the sample by 0.5% (µg/g).

The results of diacetyl content during storage are in agreement with Vahcic and Hruskar (2000) [25], in which diacetyl was found to increase slightly almost linearly on the lowest temperature (4 °C), but significantly on higher temperature levels (20 and 37 °C) during 25 days of storage (Figure 4 [25]). Our obtained higher levels of diacetyl may be explained by the adding of chufa, which components may enhance the production of diacetyl by starter organisms.

El-Shenawy et al. (2012) [31] studied the diacetyl content of probiotic yoghurt made with chufa extract, stored at 4 ±2 °C for 10 days. It was observed a gradual increase in the concentration of diacetyl until day 10, that is similar to our results. However, the initial diacetyl content of our samples is lower than obtained results by El-Shenawy et al [31]. This may be due to the different composition of the starter microorganisms. It is well known, that different starter microorganisms influence the flavour as well as the texture of the final product [25, 36].

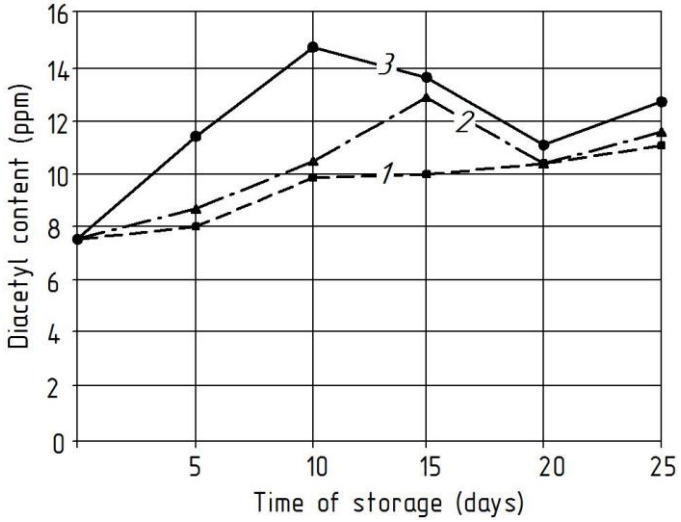

Figure 4. Diacetyl content in samples during storage [25].
Temperature: 1 – 4 °C; 2 – 20 °C; 3 – 37 °C.

3.2. Determination of acidity

The acidity of a food product is one of the first quality indices that demonstrate its freshness [22]. The results obtained for the determination of the acidity of the analyzed yoghurt samples are presented in Figure 5.

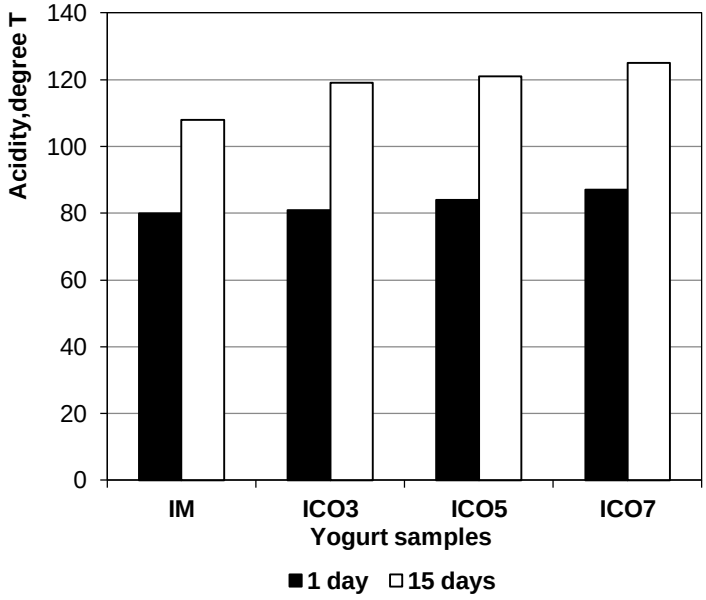

Figure 5. The evolution of the acidity of yoghurt samples

Following the determination, an increase in acidity is observed in all yoghurt samples, from day 1 to day 15. The IM sample shows acidity values between 80°T and 108°T. In the case of samples IC03, IC05 and ICO7, the addition of chufa flour contribute to the variation of the titratable acidity, the values being between 81, 84 and 87 °T on day 1 and 119, 121 and 125 °T for day 15. The evolution of the acidity for the samples with the addition of the chufa is higher than the control sample, and the sample with the highest quantity of the chufa, respectively of 0.7% presents the highest acidity for the analyzed period.

One explanation for this is that the chufa used improves the growth of bacteria contained in yoghurt samples. This increase of lactic acid bacteria may be due to the presence of some growth promoter, such as salts, free amino acids, or vitamins present in chufa [40]. Also, it has been found, that starch and fibre content of chufa presumably provides prebiotic properties for colon bacteria, as well as, yoghurt microorganisms [41]. Ire F.S., Maduka N. and Njoku H.O (2017) [42] reported that chufa milk was a possible culture medium to cultivate probiotic lactic acid bacteria such as *Lactobacillus plantarum, Lactobacillus acidophilus, Streptococcus thermophilus* and *Lactobacillus brevis.*

A similar observation was reported by [21], who reported that the acidity of the yoghurt increased due to the type of added plants. R.E.Sanful (2009) [43] obtained similar results during the investigation of chufa, cow milk and their compositions as substrates for yoghurt production.

3.3. Determination of syneresis

Syneresis is considered by many researchers as one of the most important parameters that indicate the quality of yoghurt during storage [23]. The following figure shows the changes in the syneresis rates of the yoghurt samples analyzed during the storage period.

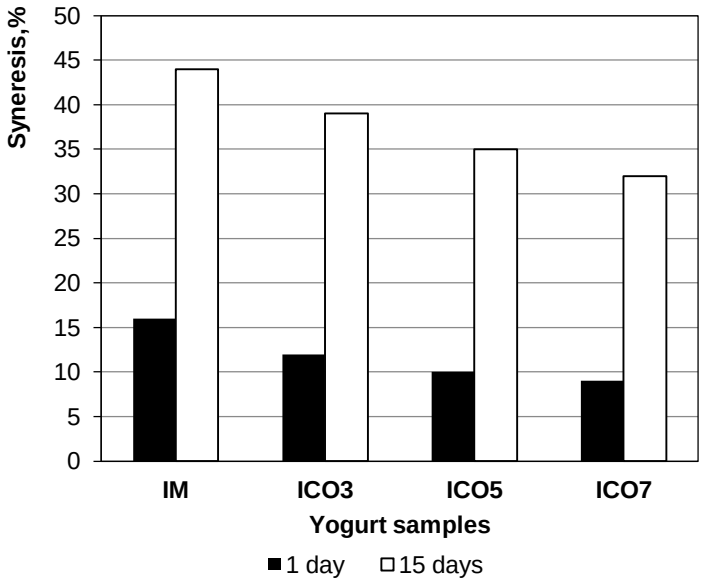

Figure 9. The evolution of the syneresis of yoghurt samples

The control sample showed a higher syneresis compared to the yoghurt samples with different levels of added chufa so that after 15 days of storage it shows elimination of whey of 44% because the dry matter content also has an influence.

In the case of samples IC03, IC05 and ICO7, the addition of chufa contribute to the syneresis process, the values being between 12, 10 and 9% respectively on day 1 and 39, 35 and 32% for day 15. The lowest syneresis after 15 days of storage was observed for chufa yoghurt with an addition of 0.7%, which demonstrates that the addition of chufa flour improves the texture of the yoghurt, and thus reduces the process of syneresis. And for this studied feature there is a similar observation which shows that syneresis is influenced by the amount of additive used [24].

The ability of yoghurt to retain whey depends on structure and pore size of protein gel [44]. Its appears that supplementation with a low level of chufa may contain some polysaccharides which enhance the water holding capacity, while supplementation with the high level impaired the yoghurt structure, thereby decreased whey syneresis. Folkenberg et al. (2006) [45] observed that syneresis was more pronounced in EPS containing yoghurts. They have suggested that yoghurts should have a structure with medium size pores containing polysaccharides to provide a stable structure with minimum syneresis. A similar observation during storage was made by Doleyres et al. (2005) [46] in yoghurts prepared using EPS-producing cultures, as well as, El-Shenawy et al. (2012) [31] in yoghurts with chufa extracts.

Conclusions

1. The characteristics of the yoghurt quality with the addition of a chufa flour were improved compared to the control sample.
2. The use of a larger amount of chufa positively influenced the parameters analyzed during storage.
3. The addition of chufa shows that it improves the quality of the yoghurt and implicitly the requirements of the consumers.

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Effect of *Spirulina platensis* and kelp on the antioxidant activity of wheat bread

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Abstract

Introduction. The effect of some edible seaweed (*Spirulina platensis* and *Kelp)* on the antioxidant activity of wheat bread was studied.

Materials and methods. Bread is obtained from wheat flour with the addition of *Spirulina platensis* and *Kelp (powder)* in the amount of 2 or 4% by the weight of flour. The antioxidant activity of ethanolic extracts was evaluated by three methods: FRAP (ferric reducing antioxidant power), DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging method and hydroxyl radical (OH) scavenging assay (HRSA).

Results and discussion Significant differences in total polyphenol content were found among different quantities of Kelp and Spirulina platensis added in breads. The highest polyphenols content had bread sample containing 4% *Spirulina platensis*: 0.88±0.02 mg GAE/g DW, and the lowest – sample with 2% *Kelp*: 0.44±0.05 mg GAE/g DW. There is a correlation between DPPH radical scavenging activities and total polyphenol and flavonoid contents. The highest DPPH radical scavenging activity was measured in *Spirulina* supplemented bread (4%) – 3.11±0.05 mmol TE/g DW. In contrast, the lowest DPPH scavenging capacities was observed in ethanol extracts from bread with 4% *Kelp* (0.89±0.02 mmol TE/g DW). Antioxidant ability of ethanol extracts for reducing Fe^{3+} by the FRAP values reflecting the ranged from 2.77 (for the sample with 4% *Kelp*) to 5.04 μmol Fe^{2+}/g DW (for the sample with 4% *Spirulina*). With an increased *S. platensis* concentration, significant changes were noted in the hydroxyl radical scavenging activity. The highest values were 27.8±0.4 μg BHT/g DW in the sample prepared with 4% *Spirulina platensis*, and 17.16±0.42 μg BHT/g DW in the bread containing 2% of the same algae. The result for the control sample was 13.85±0.37 μg BHT/g DW – higher value than the sample with 2% *Kelp* (11.85±0.42 μg BHT/g DW) and 4% *Kelp* (7.94±0.34 μg BHT/g DW), as with other two methods for determining the antioxidant activity.

Conclusions Ethanol extracts from bread prepared with the addition of 4% *Spirulina platensis* had the highest content of phenolic compounds and antioxidant activity measured with all the methods used.

Introduction

Oxidative stress can be defined as an excessive amount of reactive oxygen species (ROS), which is result of an imbalance between their production and destruction [2]. Different authors [1, 3, 4] point that oxidative stress causes irreversible damage to protein, lipid and DNA that are involved in pathogenesis of major diseases such as cardiovascular disease, cancer, diabetes, neurological disorders, atherosclerosis, hypertension, ischemia/perfusion, acute respiratory distress syndrome, asthma and also aging. So different ways to reduce the oxidative stress need to be pointed out.

It is well known that lifestyle and nutrition might play an important role against environmental oxidant exposure and damage. One of the possibilities for prevention is the ingestion of protective ingredients from food, with dietary components having been reported to show protective effects against oxidative stress [5]. These ingredients are considered to protect neuronal cells mainly via the reduction of ROS. It is worthwhile to study different patterns of nutrition and their role in preventing oxidative stress. Since oxidative damage of cells increases with age, the increased intake of exogenous antioxidants may support the endogenous antioxidative defense. Clinical studies imply that eating certain foods (such as fruits, vegetables, whole grains, products rich in omega-3 fatty acids) can help humans in decreasing oxidative stress and postponing the incidence of degenerative diseases [6]. It is of interest to study the antioxidant capacity of foods with regular and daily consumption, because a better effect would be achieved. Bread is a staple food for the population in many countries around the world. Bread made with refined wheat flour is a food with a low antioxidant capacity [8]. Therefore, enriching bread with antioxidant substances would reduce oxidative stress and improve the health status of the population as a whole.

In the last decade, many studies have demonstrated that the consumption of food enriched in antioxidants and bioactive compounds, able to counteract oxidative stress, may represent a strategic tool to maintain health and wellness and to prevent disease caused by oxidative stress [7]. Due to the huge variety of products containing natural antioxidants, it is of interest to study the optimal amounts for their use in wheat bread formulation and their effect on its antioxidant capacity. Many algae have been demonstrated to have antioxidant properties, but few studies have investigated the antioxidant activity of bread supplemented with them. In addition, little information is available regarding the relationships between the active compounds and antioxidant activities in bread made with algae.

The influence of brown algae on the antioxidant properties when added directly into gluten-free bread (GFB) recipe was determined by Różyło et al. [9]. Algae powder was added in the quantity of 2, 4, 6, 8, and 10% of the total flour content. Brown algae addition significantly increased the antioxidant activity of GFB. Most importantly, antiradical compounds from the functional products were highly bio accessible in vitro. The results confirm the possibility of the use of brown algae powder in the production of GFB. It has not been studied how this brown seaweed (*Kelp*) would affect the antioxidant capacity of gluten-containing wheat bread.

The antioxidant properties of another kind of algae – *Spirulina platensis*, are attributed to molecules such as phycocyanin, β-carotene, tocopherol, γ-linolenic acid and phenolic compounds [10]. Phycocyanin is a water-soluble pigment and the major antioxidant compound in *Spirulina* [11]. The antioxidant properties of phycocyanin of *Spirulina platensis* are related to its radical scavenging and metal chelating activities [12]. It is of interest to study the effect of *Spirulina platensis*, added in various amounts, on the antioxidant capacity of wheat bread.

Brown algae *Kelp* and blue-green algae *Spirulina platensis* contain numerous biologically active substances with a proven positive effect on human health. In many countries, a modern trend is the enrichment of various foods with these two types of algae. It is worthwhile to investigate the effect of these two types of algae added in different amounts to the wheat bread recipe, on its antioxidant capacity.

The aim of the research is to study the effect of *Spirulina platensis* and *Kelp* (added in the amount of 2% and 4%) on antioxidant activity of wheat bread.

Materials and methods

Materials

For the preparation of the bread samples, the following materials were used:

- Commercial wheat flour type 500 with the following properties: moisture content – 12.8%; gluten content – 27.07%; release of gluten – 6 mm; titratable acidity – 2 °H;
- Water – according to ISO 6107-1:2004;
- Commercial yeast (Lesafmaya);
- Salt – according to Codex Standard for Food Grade Salt CX STAN 150-1985;
- *Spirulina platensis* powder (average chemical composition: protein 64 g/100 g; fat 8.2 g/100 g of which saturated 3.42 g; carbohydrates 16.1 g/100 g, of which sugars 0.52 g, fiber 7 g/100 g).
- *Kelp* powder (average chemical composition: protein 5.3 g/100 g; fat 4.2 g/100 g of which saturated 0.9 g; carbohydrates 12.0 g/100 g, of which sugars 0.5 g, fiber 1.25 g/100 g).

Methods

Dough and bread composition

The composition of the bread samples is presented in Table 1.

Table 1

Bread samples composition

Ingredients	**Bread samples**				
	Control sample	Sample with 2% Spirulina platensis (**S2**)	Sample with 4% Spirulina platensis (**S4**)	Sample with 2% Kelp (**K2**)	Sample with 4% Kelp (**K4**)
Wheat flour (type 500), g	250	245	240	245	240
Water, cm^3	140	145	155	145	155
Yeast, g	3.37	3.37	3.37	3.37	3.37
Salt, g	3.25	3.25	3.25	3.25	3.25
Spirulina platensis, g	–	5	10	–	–
Kelp, g	–	–	–	5	10

Bread preparation

Bread is obtained from type 500 wheat flour by a two-phase method. Initially, knead the yeast, flour and water dough in a 1:1 ratio in kneading machine (Labomix 1000, Hungary). Pre-mixed *Spirulina platensis* and *Kelp* algae (powder) in the amount of 2% or 4% by the weight of flour are added to the mixing water. (combinations K2 and K4, for the breads prepared with *Kelp* and combinations S2 and S4, for the breads prepared with *Spirulina platensis*, respectively). The control sample was prepared only with wheat flour. The dough thus prepared matures for 4 hours at 33 °C and then mix the dough to obtain a homogeneous mass by adding the remainder of the flour to the formulation and salt (1.3 kg/100 kg flour). The bread dough divides (440 g) and forms, matures for 55 minutes at 38 °C (Tecnopast CRN 45–12, Novacel ROVIMPEX Novaledo, Italy). After the final fermentation, the pieces of dough were put into an electric oven (Salva E-25, Spain) pre-heated to 200–220 °C. The baking time is 24 min, until the temperature in the center of the bread crumb reach 96–98 °C. After baking, the bread is allowed to cool down for 3 h at room temperature.

Sample extraction

The extraction process of bioactive compounds from dry breads was carried out with 70% ethanol as described in Vasileva et al., 2018 [13]. Bread samples were sliced (about 1.5 cm thick), dried (40 °C, 24 h), ground in a mill, and sieved (0.5 mm sieve). Ethanol extracts from breads were obtained with 70% ethanol (solid to liquid ratio 1:20) in an ultrasonic bath (VWR, Malaysia; 45 kHz, 30 W) at 45 °C for 15 min. Samples were then centrifuged at 1800xg for 15 min (MPW-251, Med. Instruments, Poland). The supernatants were used for further studies.

Analytical methods

a. Total polyphenols were quantified by using Folin-Ciocalteu's reagent (Ainsworth and Gillespie, 2007) [14]. Gallic acid was employed as calibration standard and the results were expressed as mg equivalents gallic acid (GAE) per gram dry weight (DW).

b. Total flavonoids were determined using $Al(NO_3)_3$ reagent and measuring the absorbance at 415 nm according to Kivrak et al., 2019 [15]. The results were expressed as mg equivalents quercetin (QE) per gram DW.

c. In vitro antioxidant activity determination

The antioxidant activity of ethanolic extracts was evaluated by three methods: FRAP (ferric reducing antioxidant power), DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging method and hydroxyl radical (OH·) scavenging assay (HRSA).

1. FRAP (Ferric Reducing Antioxidant Power) method

The FRAP method is based only on single electron transfer mechanism and was measured according to the method of Dimov et al. [16] with some modification. Three ml freshly prepared FRAP reagent (10 parts 0.3 M acetate buffer (pH 3.6), 1 part 10 mM 2,4,6-tripyridyl-s-triazine (TPTZ) in 40 mM HCl and 1 part 20 mM FeCl3.6H2O in d. H_2O) were mixed with 0.1 ml of investigated ethanolic extract. The reaction time was 10 min at 37 °C in darkness and the absorbance was measured at 593 nm against blank prepared with 70% ethanol. A standard curve was built with $FeSO_4.7H_2O$. The results of FRAP analysis were expressed as μmol Fe^{2+} equivalents per gram DW (Irshad et al., 2012) [17].

2. DPPH radical scavenging assay

The DPPH radical method is based on mixed hydrogen atom transfer and single electron transfer mechanisms.

DPPH radical scavenging activity was estimated according to Dimov et al., 2018 [16] with some modification. Briefly, 0.15 ml of ethanolic extract was mixed with 2.85 ml 0.06 mM DPPH fresh solution in 96% ethanol. The mixture was left for 30 min (kept in the dark at room temperature) so that a reaction could take place, and then the absorbance at 517 nm was read by spectrophotometer in comparison to the blank containing 70% ethanol. The results of DPPH analysis were expressed as mmol Trolox equivalents (TE) per gram DW.

3. Hydroxyl radical scavenging assay (HRSA)

The scavenging activity for hydroxyl radicals was measured with Fenton reaction with a few modifications (Jin et al., 1996) [18]. OH· could oxidize Fe^{2+} into Fe^{3+}, and only Fe^{2+} could combine with 1,10-phenanthroline to form a red colored complex with the maximum absorbance at 536 nm. The concentration of hydroxyl radical was determined by the degree of decolourization of the reaction solution. The reaction mixture contained 1 ml of 0.75 mM 1,10-phenanthroline, 2 ml of 0.2 M phosphate buffer (pH = 7.4), 1 ml of 0.75 mM $FeSO4 \cdot 7H_2O$, 1 ml H_2O_2 (0.01% v/ v), and 1 ml of investigated ethanolic extract was incubated at 37 º for 60 min in a water bath. The absorbance of reaction mixture was measured at 536 nm against reagent blank. The results of HRSA were expressed as μg BHT (3,5-Di-tert-4-butylhydroxytoluene) per gram DW.

Statistical analysis

Results are presented as means of at least three independent determinations±standard deviation (SD). Statistical evaluation was performed by using one-way analysis of variance (ANOVA) of the IBM SPSS Statistics program (Somers, NY, USA). Mean differences were established by Fisher's least significant difference test for paired comparison with a significance level $\alpha = 0.05$.

Results and discussion

Determination of total polyphenol and flavonoid contents

Due to the variety of bioactive compounds contained in algae and their differing solubility properties in different solvents, the optimal solvent for extraction depends on the particular algae materials, and the compounds that are to be isolated [19, 20]. According to Poole et al. [21], 75% ethanol aqueous solution, nearly doubled the polyphenol yield when compared to extraction with water alone. Based on this background and many other reports, in the present study, we employed extraction of bioactive compounds from the breads using ultrasound and 70% ethanol as a good extraction solvent. We evaluated the in vitro antioxidant properties of the 70% ethanol extracts and correlated their antioxidant activities with 2,2-diphenyl-1-picrylhydrazyl (DPPH method), ferric reducing antioxidant power (FRAP method) and hydroxyl radical scavenging activities (HRSA). In addition, we determined the total polyphenol and flavonoid contents in the different types of bread, i.e. phenolic compounds are considered to be dominant contributors to the antioxidant activity and also possess many biological activities.

Polyphenols serve as powerful antioxidants due to the hydrogen-donating ability of their hydroxyl groups as well as their ability to donate electrons to arrest the production of free radicals as a result of oxidative stress [22]. Flavonoids are the largest class of polyphenols.

The total polyphenol and flavonoid contents of ethanol extracts from bread samples prepared with 2% and 4% *Kelp* (K2 and K4), and 2% and 4% *Spirulina platensis* (S2 and S4) are presented in Table 2.

Table 2

Comparison of total polyphenol and flavonoid contents in ethanol extracts

Ethanol extracts	Total polyphenol, mg GAE/g DW	Total flavonoids, mg QE/g DW
Control	0.68±0.01[c]	0.13±0.00[c]
K2	0.52±0.03[d]	0.11±0.00[d]
K4	0.44±0.05[e]	0.10±0.00[e]
S2	0.74±0.01[b]	0.20±0.00[b]
S4	0.88±0.02[a]	0.28±0.00[a]

Note: DW – dry weight bread.

The results were expressed as mean±SD (n=3).

[a-e] Means in a column with different superscripts differ significantly ($p<0.05$).

Significant differences in total polyphenol content were found among different quantities of *Kelp* and S*pirulina platensis* added in breads. The addition of *S. platensis* (2 and 4%), compared to the control sample generally increased the polyphenol content in breads. The highest polyphenols content had S4: 0.88±0.02 mg GAE/g DW. The difference between the values of the control sample and samples S2 and S4 expressed as percentage increase were 9% and 29%, respectively. Cozmuta et al. [23] reported similar results for higher level of polyphenols in the bread enriched with *Spirulina* powder. By increasing the amount of incorporated *Spirulina* with 1%, 3% and 5%, the polyphenols content rises 1.19-fold, 1.41-fold and 2.73-fold, compared to control bread. Increased polyphenols content of breads was also observed by Saharan and Jood [24], while investigating antioxidant activity of bread enriched with 2, 4 and 6% *S. platensis* powder.

A reduction in the polyphenol content with the increase of the quantity of *Kelp* (2% and 4%) added in bread was observed, compared to control sample. The lowest level in the polyphenols content had K4: 0.44±0.05 mg GAE/g DW. The difference between the values of the control sample and samples K2 and K4 expressed as percentage reduction were 24% and 35%, respectively.

The same order of total flavonoids was obtained. Total flavonoids of control sample were: 0.13 mg QE/g DW (19% of the content of the total polyphenols), K2 – 0.11 mg QE/g DW (21% of the content of the total polyphenols), K4 – 0.10 mg QE/g DW (23% of the content of the total polyphenols), S2 – 0.20 mg QE/g DW (27% of the content of the total polyphenols), S4 – 0.28 mg QE/g DW (32% of the content of the total polyphenols). Overall, the total polyphenols and flavonoids were in the order S4>S2>Control sample>K2>K4.

Seghiri et al. [25] used absolute methanol for extraction of polyphenols and flavonoids from *S. platensis* biomass and reported very low yield of polyphenols – 0.29 mg GAE/g DW. However, the amount of extracted flavonoids is higher than in our research – 58% of the content of the total polyphenols (0.17 mg QE/g DW).

Determination of antioxidant activity

Antioxidant activity is a complex procedure usually happening through several mechanisms and is influenced by many factors, which cannot be fully described with one single method [26]. Therefore, it is essential to perform more than one type of antioxidant capacity measurement to take into account the various mechanisms of antioxidant action [27 – 29]. In this study, the antioxidant properties of ethanol extracts from breads prepared with *Kelp* and *Spirulina platensis* in different concentration (2 and 4%) were determined by DPPH, FRAP, and hydroxyl radical scavenging assays (HRSA), and were compared with the control sample (made with white flour, 0% algae). Antioxidant potentials of the samples varied with species of algae and the quantity imported into flour.

DPPH assay is one of the most popular and frequently employed methods among antioxidant assays. The method is simple, efficient, relatively inexpensive, and quick [30]. The method is based on the reduction of DPPH, a stable free radical [31]. The free radical DPPH with an odd electron gives a maximum absorption at 517 nm (purple colour). When antioxidants react with DPPH, which is a stable free radical becomes paired off in the presence of a hydrogen donor (e.g., a free radical-scavenging antioxidant) and is reduced to the DPPHH and as consequence the absorbance's decreased from the DPPH [32]. Radical to the DPPH-H form, results in decolorization (yellow colour) with respect to the number of electrons captured [33]. More the decolorization more is the reducing ability [34].

The DPPH radical scavenging activity of the ethanol extracts is shown in Figure 1.

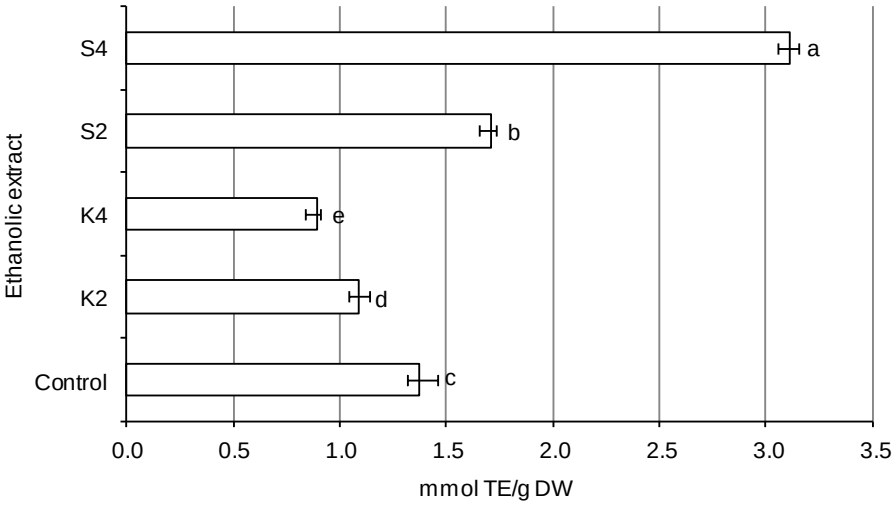

Figure 1. DPPH radical scavenging activity (mmol TE/g DW) of ethanol extracts
[a-e] Means with different lowercase letters differ significantly ($p<0.05$).
Note: DW – dry weight bread.

The results of our work indicate a correlation between DPPH radical scavenging activities and total polyphenol and flavonoid contents. The DPPH radical scavenging activity of S2 and S4 increased in a concentration-dependent manner, and the highest value was 3.11±0.05 mmol TE/g DW in S4, followed by S2 – 1.71±0.03 mmol TE/g DW. In contrast, the lowest DPPH scavenging capacities were observed in ethanol extracts received from bread with 4% *Kelp* – K4 (0.89±0.02 mmol TE/g DW) and 2% *Kelp* – K2 (1.09±0.05 mmol

TE/g DW). Both K2 and K4 had lower DPPH radical scavenging activity than the control sample (1.37±0.09 mmol TE/g DW), as that decrease is in a concentration-dependent manner, too. This can be explained by the baking at high temperature (200–220 °C), which may destroy some bioactive compounds in *Kelp* algae and decrease the inhibition of DPPH radical scavenging activities.

Our results are in agreement with the findings of El Baky et al. [35] and Singh et al. [36], considering that the antioxidant capacity increases with the increasing levels of *S. platensis* in bread. Cozmuta et al. [23] reported similar results for higher antioxidant activity (by DPPH method), after the addition of 1%, 3% and 5% *S. platensis* in the bread. It increased to 11.06% in bread with 1% *S. platensis*, 13.21% in bread with 3% *S. platensis* and 15.46% in bread with 5% *S. platensis* from 10.24% in control bread.

The incorporation of 6% and 10% *S. platensis* in "crostini" led to a significant increase in DPPH radical scavenging capacity, compared to the control [37] sample.

Increased antioxidant capacity (by DPPH method) was also observed by Saharan and Jood [24], while investigating breads enriched with 2, 4 and 6% *S. platensis* powder. Maximum antioxidant activity they observed in 6% *Spirulina* supplemented bread.

Carp and barbel burgers containing 1% of *Spirulina* showed significantly higher DPPH scavenging activities (86.76% and 94.09%, respectively) than control burgers (56.28% and 40.09%) [38].

FRAP method. The method is based on the reduction of Fe^{3+} TPTZ complex (colorless complex) to Fe^{2+}-tripyridyltriazine (blue colored complex) formed by the action of electron donating antioxidants at low pH [39]. The results of our work indicate a correlation between the reducing power determined by FRAP method, DPPH radical scavenging activity, and total polyphenol and flavonoid contents. Antioxidant ability of the ethanol extracts for reducing Fe^{3+} by the FRAP values reflecting the ranged from 2.77 to 5.04 μmol Fe^{2+}/g DW (Figure 2).

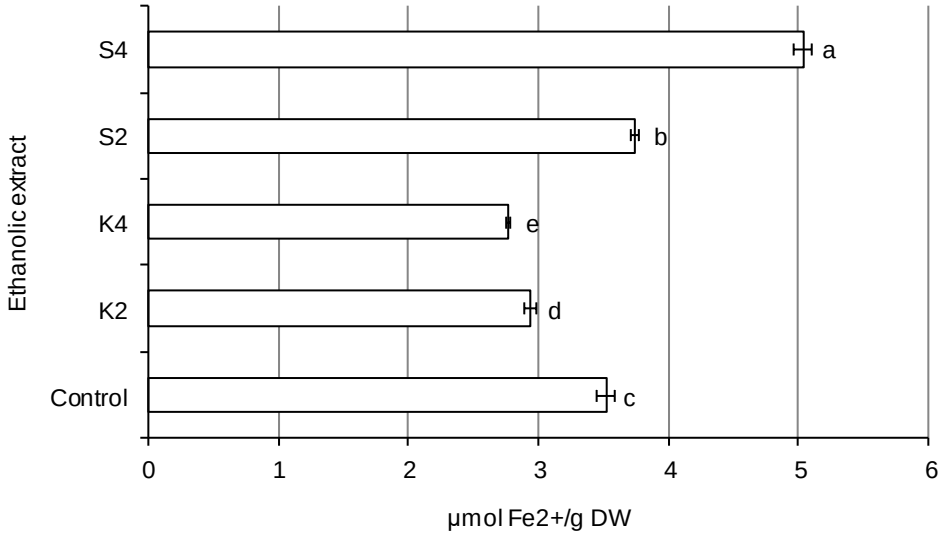

Figure 2. Ferric Reducing Antioxidant Power (μmol Fe^{2+}/g DW) of ethanol extracts
[a-e] Means with different lowercase letters differ significantly ($p<0.05$).
Note: DW – dry weight bread.

FRAP assays varied significantly among species. The sample S4 showed the highest mean FRAP (5.04±0.07 μmol Fe^{2+}/g DW), followed by S2 (3.75±0.03 μmol Fe^{2+}/g DW), control sample (3.52±0.07 μmol Fe^{2+}/g DW), K2 (2.94±0.04 μmol Fe^{2+}/g DW) and K4 (2.77±0.02 μmol Fe^{2+}/g DW). Our results contradict the results of another team of authors [40], and according to them brown algae *E. arborea* had higher FRAP value (11.9 μmol $FeSO_4$ μg^{-1}) than the red *A. spicifera* (9.8 μmol $FeSO_4$ μg^{-1}), and the green *R. intrincata* had the lowest FRAP value mean (2.6 μmol $FeSO_4$ μg^{-1}).

The reducing power of the ethanol extracts from *Spirulina*-containing breads may serve as a significant indicator of its potential antioxidant activity. This activity may be due to phenolic compounds and flavonoids present in the extract as also indicated by Velioglu et al. [41].

Carp and barbel burgers containing 1% of *Spirulina* showed significantly higher ferric reducing activity (0.615 and 0.584 is absorbance at 700 nm, respectively) than control burgers (0.315 and 0.410 is absorbance at 700 nm) [42] as in our work with *Spirulina*-breads.

Hydroxyl radical scavenging assay (HRSA). The hydroxyl radical is the most reactive free radical and can be formed from superoxide anions and hydrogen peroxides in the presence of metal ions, such as copper and iron. Hydroxyl radicals can cause damage to nearly all types of biomolecules, including proteins, DNA, polyunsaturated fatty acids, and nucleic acids [43]. The scavenging effect of OH was investigated using the Fenton reaction and the results are shown in Figure 3.

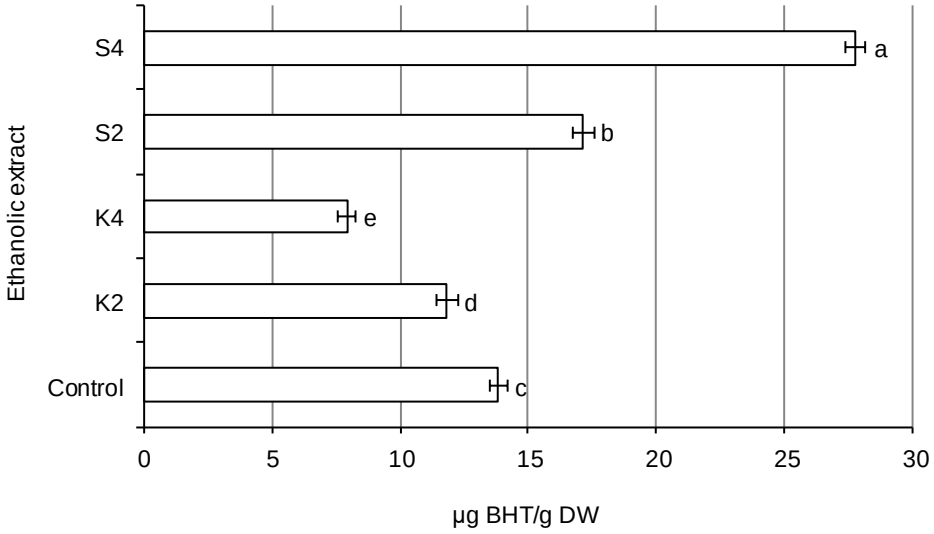

Figure 3. Hydroxyl radical scavenging activity (μg BHT/g DW) of ethanol extracts
[a-e] Means with different lowercase letters differ significantly ($p<0.05$).
Note: DW – dry weight bread.

With an increased content of *S. platensis* concentration, significant changes were noted in the Hydroxyl radical scavenging activity. The highest values were 27.8±0.4 μg BHT/g DW in S4, and 17.16±0.42 μg BHT/g DW in S2. Singh et al. [36] found a linear positive

correlation between *S. platensis* concentration (from 1.6 to 8.4%) in biscuits and antioxidant activity. The control sample showed the same trend (13.85±0.37 μg BHT/g DW) – higher value than K2 (11.85±0.42 μg BHT/g DW) and K4 (7.94±0.34 μg BHT/g DW), as with other two methods for determining the antioxidant activity. The results of our work indicate a correlation between Hydroxyl radical scavenging activity, the reducing power determined by FRAP method, DPPH radical scavenging activity, and total polyphenol and flavonoid contents.

Discussion

The use of *S. platensis* in the food industry has been reported by many authors. *Spirulina* can be supplemented to noodles, breads, biscuits, candies, ice cream, bean curd etc. as food additives to enhance nutritive and health values [44]. *Spirulina* extracts are used to enrich liquid foods such as health drink, soft drink, tea, beer or spirits [21]. Powder can be used in a variety of food products like soups, sauces, pasta, snack foods, instant drinks and other recipes. Extraction methods can be used to obtain discoloured *Spirulina* powder (yellow-white) which is odorless and tasteless, and thus suitable for widespread use [45]. Herero et al. [46] recommended that ethanol rather than other solvents should be used for the extraction of antioxidants from *Spirulina*, as it is regarded as Generally Recognized as Safe (GRAS), if the extracts are to be used as a functional ingredient in the food industry.

According to Omidi et al. [47], S*pirulina*-containing pasta had a higher phenolic content and an antioxidant activity than the control pasta. El Baky et al. [35] observed increasing antioxidant activity for biscuits containing *S. platensis* biomass (from 0.3 to 0.9%). Bolanho et al. [48] reported that the addition of 5% *S. platensis* to formulations of cookies increase content of protein, fiber, ash, total phenolic compounds and antioxidant capacity. They showed an increase of about 65% (from 1.4 to 2.3 mg GAE g^{-1}) in total phenolic content in 5% *S. platensis* cookies when compared to the control sample. Barkallah et al. [38] tested the addition of 1% *Spirulina* in carp and barbel burgers and found a significant increase in their antioxidant activities, compared to the control burgers.

Many studies have demonstrated high antioxidant potential of brown seaweed [49 – 52]. The bioactive properties are mainly due to the presence of phlorotannin [53], a type of polyphenol (secondary metabolite) [54]. *Ascophyllum nodosum* (*Kelp*) is one of the brown algae species with the highest concentrations of phlorotannin (9–14% of its dry weight, depending on seasonal variability) [55]. Phlorotannins have received increasing interest because of their antioxidant, anti-wrinkling, antiallergic, anti-cancer, and hair growth-promoting abilities [56–58]. These characteristics make brown seaweed a useful and valuable ingredient for functional foods [59].

Research on bakery products with brown algae is scarce. The only study focused on the antioxidant activity of bread supplemented with brown algae was published by Rózylo et al. [9]. According to them, the addition of brown algae in bread leads to significant increase in bioactive properties. But, the results obtained by us for the polyphenol and flavonoid contents, and antioxidant activity of the ethanolic extracts from breads prepared with two *Kelp* concentrations (2% and 4%) were unexpected.

This could be partially explained by the phlorotannin concentration. It reacts to the algae's external conditions, such as light, temperature, and biotic stressors, as well as sample handling and preservation methods [21]. Studies have shown that phenolic concentration monitored over a year in one brown algae species found that yields differed seasonally [60].

According to Poole et al. [26], lower phenolic content is the result of sun exposure likely causes a degradation of phlorotannins. Cruces et al. [61] and Esteban et al. [62] made similar

conclusion. They observed that drying processes that require longer time lengths to dehydrate the seaweed samples tended to have a loss in phlorotannins and antioxidant capacity due to degradation and oxidation. These suggestions likely explain why the breads prepared with *Kelp* have lower bioactivity, compared to control sample.

According to Mekini´c et al. [63], the solubility of the bioactive compounds is governed by the type of solvent used, degree of polymerization and their interactions with other food constituents what leads to formation of insoluble complexes.

According to Velioğlu et al. [41], different baking processes used to produce different products (breads, cookies and cakes, contained equal amount of hazelnut testa in the formulation), significantly affect the amount of phenolics.

On the other hand, polyphenols content varies depending on the efficiency of the extraction method [21]. For example, some compounds, such as water-soluble polysaccharides, protein and organic acids are simultaneously extracted when using water alone as the extraction solvent [65]. Lopez et al. [66] compared the phenolic contents and antioxidant activity of the water, water/methanol (1/1), methanol and ethanol extracts from the brown seaweed *Stypocaulon scoparium* and found that the aqueous extracts showed the highest phenolic content and antioxidant activity. So that, used to our work 70% ethanol may not be sufficiently effective to extract bioactive components of bread made with *Kelp*.

Conclusion

Ethanol extracts from breads prepared with *Spirulina platensis* exhibited high antioxidant activity. The bread prepared with 4% *Spirulina platensis* showed the highest content of the phenolic compounds and antioxidant activity with all the methods used. With an increased content of brown algae, significant changes were noted down in the content of the phenolic compounds and antioxidant activities. Their values decreased significantly with increasing brawn algae addition (in the range of 2–4%). There is a positive correlation between total polyphenol and flavonoid contents, and the antioxidant activity determined by FRAP method, DPPH method, and Hydroxyl radical scavenging assay. This correlation indicates that the phenolic compounds largely contribute to the antioxidant activities of these algal species.

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Rheological studies of berry sauces with iodine-containing additives

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Abstract

Introduction. The purpose of the research: to establish the influence of the addition of seaweed raw materials and the absence of structure-forming agent on the rheological parameters of berry sauces.

Materials and methods. Materials of rheological studies were samples of blueberry-cranberry sauce with guelder rose juice with different content of hydrated seaweed and control samples with modified corn starch and xanthan gum. The research of rheological properties was carried out rotational viscometer. Sensory research of sauces was performed on a five-point scale based on the weighting factor.

Results and discussion. The curves of the effective viscosity on the shear rate of the test specimens are similar to the curves of the control samples in all series of tests. The use of Fucus seaweed increases the viscosity of wild berry sauces without additional structuring agents compared to control samples made from xanthan gum, which is equal for samples with Fucus – 7.32 Pa·s, with xanthan gum – 7.22 Pa·s. The use of seaweed instead of xanthan gum and starch improves the ability of macroscopic systems to independently restore the structure after its destruction, as evidenced by relatively larger values of thixotropy coefficients, namely, the thixotropy coefficient for samples with xanthan gum is – 56.9%, with starch – 64%, with Laminaria – 78.0%, with Undaria pinnatifida – 82.0%. The use of seaweed improves the structural properties of pasteurized objects, which is confirmed by a decrease in the value of the coefficient of consistency, proportional to the viscosity of the sauce samples compared to non-pasteurized samples – for samples with Undaria pinnatifida by 0.84 Pa·s, with Laminaria by 0,20 Pa·s. Addition of up to 8% Laminaria and 3% Fucus and Undaria pinnatifida to hydrated algae does not have a negative effect on organoleptic and rheological parameters.

Conclusions. The possibility of production of berry sauces without additional addition of structure forming agents to the recipe is proved**.**

Introduction

It is necessary to pay special attention to the structure and mechanical properties of the finished product when developing a quality sauce technology [2], in particular on vegetable raw materials [3]. As practice shows, in order to get a sauce with certain rheological properties, it is necessary to use structure-forming agent [1]. In the technologies of fruit and berry sauces, thickeners, for the most part, starches, gums etc., are the structure-forming agents [4]. Although most of them have a positive effect on the structural and mechanical properties of sauces and are widespread [5], they also have high calories and low digestibility [6]. Therefore, adding them only increases calories and does not increase the nutritional value of the product [7].

Currently, there are a number of developments of replace traditional thickeners in the production of sauce products [8]. Works on the use of modifications of starches [9–12] and composite mixtures have become the most widespread [13]. In addition, there are a number of developments that prove the feasibility of using thickeners of non-starch nature [15–19] and pectin substances [20] as structure forming agents.

However, during the analysis of existing developments, no studies were found that would confirm the possibility of not using additional thickeners in the production of berry sauces. Thus, the question of the possibility of producing sauces only on a natural basis remains unresolved.

It is known that the berry raw material contains a significant amount of pectin substances [21], which are able to have a structure-forming effect [22]. Therefore, it can be assumed that the additional introduction of thickeners in the formulations of berry sauces is not necessary. In this way, a product will be obtained that is characterized by naturalness and easily digestible.

The analysis of recent research and the relevance of the development of technology of sauces from wild and cultivated berries with the addition of iodine-containing additives has been described and proven in previous studies [23–25].

The purpose of the research: to establish the influence of the addition of seaweed raw materials and the absence of structure-forming agent on the rheological parameters of sauces.

To achieve this purpose, a number of tasks were formulated, namely:

- Development of sauce technology with high sensory quality indicators,
- To determine the effect of thickener on the viscosity,
- To determine the effect of thickener on the restoration of the structure,
- The effect of pasteurization on the viscosity of the objects of research.

Materials and methods

Materials of researches were samples of blueberry-cranberry sauce with guelder rose juice and control samples.

As the control samples, sauces of industrial production were used, namely blueberry sauce based on modified corn starch and cranberry sauce based on xanthan gum.

The technology of production of blueberry-cranberry sauce with guelder rose juice consists in mechanical culinary processing of initial raw materials, crushing of berries, preparation of seaweed raw materials, connection of components of mix, mixing before uniform distribution of components, thermal processing and pasteurization at a temperature of 98...100°C. The ratio of the main prescription components after mechanical culinary processing is bilberry puree: cranberry puree: guelder rose juice: sugar = 1:1:1/5:1. It should be noted that the developed technology does not use additional structure forming agent. The proposed sauce technology involves the use of dry seaweed. Since the hygroscopicity of seaweed is not the same, the optimal hydromodules are established: for Laminaria – 1:5–1:6, for Undaria pinnatifida – 1:8–1:9, for

Fucus – 1:3–1:4. Namely, previous studies [26], which relied on iodine content in seaweed raw materials established the possibility of adding hydrated seaweed in quantities of 3, 5 and 8% of the original recipe mass. The estimated amount of iodine in the finished sauces is 0.1–1.0 mg per 100 g of the finished sauce, depending on the type of seaweed used. This sauce is completely natural and do not contain any additional structure forming components.

Samples were studied without the addition of seaweed raw materials and with the addition of Laminaria, Fucus and Undaria pinnatifida, which in the context of the studies can be conditionally taken into account by thickeners.

Even at the initial stage of rheological studies, it became apparent that sauce samples to which hydrated Laminaria was added to the composition showed a dependence of effective viscosity on the sliding velocity similar to the control samples. At the same time, the curves of the dependence of the effective viscosity on the sliding velocity of the test samples, to which 5 and 8% hydrated Fucus and Undaria pinnatifida seaweed were added, have a different dynamics compared to the control specimens. Thus, due to the expediency of detecting the maximum amount of seaweed raw material that can be added to the sauce recipe, a series of studies with the content of hydrated seaweed Fucus and Undaria pinnatifida−3% and Laminaria − 8% are further described.

Order of research consisted of two main stages – sensory quality assessment and rheological research.

Sensory researches of sauces were performed on a five-point scale based on the weighting factor [27]. During the organoleptic analysis, the appearance, consistency, color, taste and smell were determined. For a more detailed study, each group of indicators was divided into segments. When assessing the appearance and consistency of the sauce, homogeneity, absence of inclusions, fluidity and density were determined. When assessing color – homogeneity, expressiveness, naturalness and intensity; taste – expressiveness, balance, speed of release, purity, naturalness; smell – expressiveness, compliance with the type of raw materials used, stability, purity.

The next stage of the research was to conduct **rheological researches** that would confirm the assumptions about the non-use of structure forming agent.

The research of rheological properties was carried out by an experimental method using «Reotest-2» rotational viscometer [28]. During the experiments for the sauce samples, the dependencies between the viscosity and the shear rate were recorded for different values of the strain rate from 0.3333s^{-1} to 437.4s^{-1} at 20 °C. All dependencies were recorded with increasing and decreasing velocity gradient, i.e. with forward and reverse strokes of the viscometer. The experimental conditions were as close as possible to the production conditions [29].

The effective (dynamic) viscosity of the test samples is generally described by the equation of the following form [30]:

$$\eta_{ef} = B \cdot \gamma^{-m}, \quad (1)$$

where η_{ef} – effective viscosity, Pa·s, B – coefficient of consistency proportional to the viscosity, Pa·s, γ – sliding velocity, m – rate of destruction of the structure.

The thixotropy coefficient was calculated by the formula:

$$\lambda_m = \frac{B_з}{B_n} \cdot 100, \quad (2)$$

where λ_m – thixotropy coefficient, %; $B_з$ – value of the coefficient of consistency proportional to the viscosity at reverse course, Pa·s; B_n – value of the coefficient of consistency proportional to the viscosity at forward course, Pa·s.

Results and discussion

Determination of sensory properties

The first stage of the study was the conduct of sensory analysis, which allowed determining the patterns of formation of sensory indicators, as it is on these indicators that potential consumers, in the first place, evaluate the product.

Taking into account the influence on sensory quality indicators, the possible percentage of added hydrated seaweed to the prescription composition was investigated. In previous studies, we have identified that the addition of 3–8% hydrated Laminaria, Fucus and Undaria pinnatifida does not worsen the sensory parameters [26]. The results of sensory analysis are shown in Table 1.

Table 1

Sensory analysis of sauces

Indicator	Weighting factor	Weighting factor of characteristic	Characteristic	Score, points		
				Bilberry-cranberry sauce with guelder rose juice	Bilberry sauce with Starch	Cranberry sauce with xanthan gum
Appearance	0,2	0,83	Homogeneity	4,80	4,80	4,90
		0,17	Absence of inclusions	4,80	4,70	4,70
Total score on the indicator				0,96	0,95	0,96
Consistency	0,25	0,4	Fluidity	4,90	4,70	4,80
		0,3	Density	4,70	4,80	4,70
Total score on the indicator				1,20	1,19	1,19
Color	0,15	0,3	Homogeneity	4,80	4,70	4,80
		0,2	Expressiveness	4,90	5,00	4,90
		0,2	Intensity	5,00	5,00	5,00
		0,3	Naturalness	5,00	4,90	4,90
Total score on the indicator				0,74	0,74	0,74
Taste	0,25	0,1	Expressiveness	5,00	4,70	4,80
		0,2	Balance	4,90	4,00	4,10
		0,1	Speed of release	4,80	4,00	3,90
		0,3	Purity	5,00	3,90	4,00
		0,3	Naturalness	5,00	3,90	3,80
Total score on the indicator				1,24	1,03	1,03
Smell	0,15	0,3	Expressiveness	4,90	4,80	4,90
		0,2	Compliance with the type of raw materials used	4,90	3,70	4,90
		0,2	Stability	5,00	4,70	4,80
		0,3	Purity	5,00	4,00	3,90
Total score on the indicator				0,74	0,65	0,65
Common score				4,88	4,57	4,57

The sauce recipe, which is made according to the proposed technology, does not include flavorings. Sauces are made only on a natural basis, which has a positive effect on sensory characteristics. As can be seen from the table, industrial samples of sauces, which include a significant number of additives, are almost not inferior to the developed sauces in terms of appearance, but significantly inferior in terms of taste and smell.

Influence of the type of thickener on the viscosity of berry sauces

The first series of research identified the effect of the type of thickener on the viscosity of the objects of research. The curves of the dependence of the effective viscosity of the test samples on the sliding velocity are shown in Figure 1.

The results of mathematical processing of the experimental data from Figure 1 are shown in Table 2.

The calculated values of the coefficients of determination (R^2) indicate the high reliability of the analytical equations that describe the behaviour of each of the test samples.

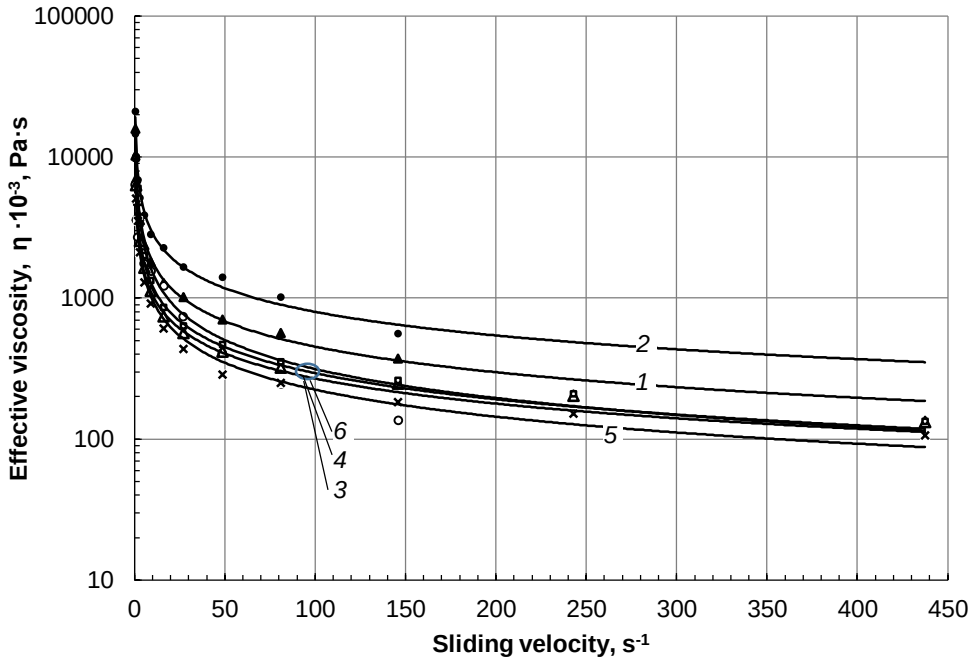

Figure 1. Dependence of the effective viscosity of the samples on the sliding velocity
1 − Sauce with Xanthan gum, 2 − Sauce with Starch, 3 − Sauce Without thickener,
4 − Sauce with Laminaria, 5 − Sauce with Undaria pinnatifida, 6 − Sauce with Fucus

Table 2

Equation coefficients (1)

Sample	***B*, Pa·s**	***m***	R^2
Sauce with Xanthan gum	7,22	0,60	0,99
Sauce with Starch	10,39	0,56	0,99
Sauce Without thickener	4,09	0,59	0,96
Sauce with Laminaria	5,00	0,62	0,99
Sauce with Undaria pinnatifida	4,19	0,64	0,98
Sauce with Fucus	7,32	0,68	0,98

According to the decrease in the value of the coefficient of consistency proportional to the viscosity, the test samples can be arranged in the following ranked row: Sauce with Starch → Sauce with Fucus → Sauce with Xanthan gum → Sauce with Laminaria → Sauce with Undaria pinnatifida → Sauce Without thickener. As can be seen from the above data, the lowest coefficient of consistency is observed in the test samples without thickener and with Undaria pinnatifida. The largest is in samples with starch and Fucus. The values of the consistency coefficients of other samples occupy an intermediate position. It should be noted that using as a thickener Fucus increases the viscosity of the target products compared to Xanthan gums (the control sample).

According to the decrease in the value of the rate of destruction of the structure, the test samples can be arranged in the following ranked row: Sauce with Fucus → Sauce with Undaria pinnatifida → Sauce with Laminaria → Sauce with Xanthan gum → Sauce Without thickener → Sauce with Starch. Samples with starch and Without thickener are characterized by the lowest rate of structure destruct ion. The structure of samples with Fucus and Undaria pinnatifida is most rapidly destroyed.

The results obtained can be primarily explained by the chemical composition of berry and seaweed raw materials. It is known that the viscosity of products, in addition to pectin, is significantly affected by other polysaccharides, including alginates [31]. According to the literature, the highest content of alginate among these algae is in fucus, the lowest – in Undaria pinnate [32, 33]. In addition, the viscosity can be affected by fucoidans, the content of which in Fucus is 9–11% on dry matter [34], in Laminaria – 2–4% [35], in Undaria pinnatifida – 5–16% [36].

Effect of thickener type on the restoration of the structure of berry sauces

The second series of experiments was aimed at determining the effect of the type of thickener on the ability of macroscopic systems to self-restore the structure after its destruction. For this purpose, the viscosity of the samples was investigated using the "reverse course" method. The curves of the dependence of the effective viscosity of the test specimens from the sliding velocity at reverse course are shown in Figure 2.

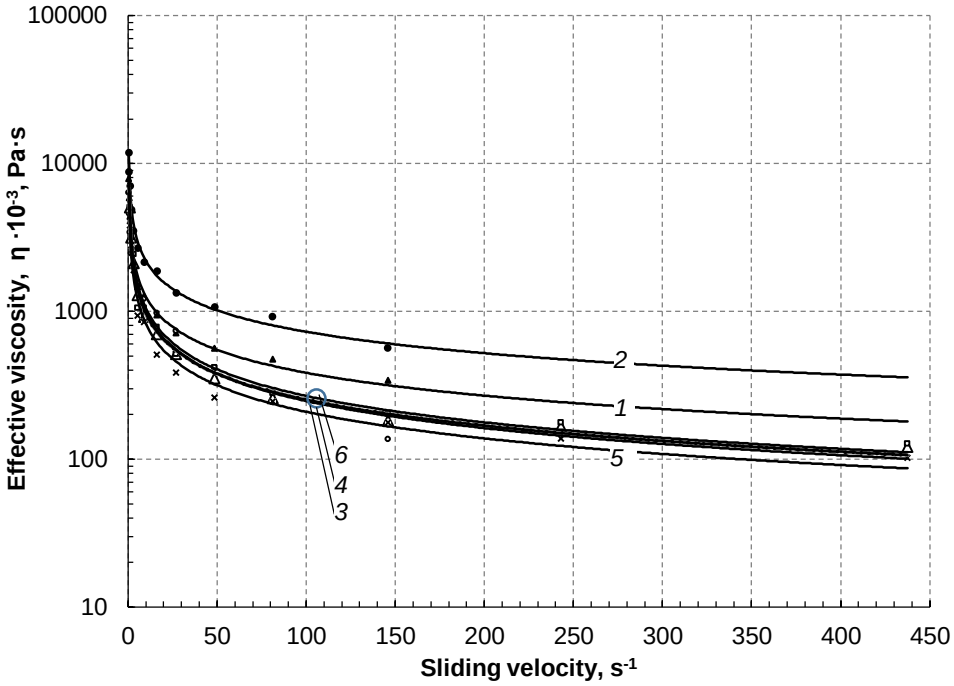

Figure 2. Dependence of the effective viscosity of the samples on the sliding velocity at reverse course

1 − Sauce with Xanthan gum, 2 − Sauce with Starch, 3 − Sauce Without thickener, 4 − Sauce with Laminaria, 5 − Sauce with Undaria pinnatifida, 6 − Sauce with Fucus

The results of mathematical processing of the experimental data from Figure 2 are shown in Table 3.

Table 3

Equation coefficients at reverse course

Sample	***B*, Pa·s**	***m***	R^2
Sauce with Xanthan gum	4,11	0,52	0,99
Sauce with Starch	6,65	0,48	0,99
Sauce Without thickener	3,22	0,56	0,93
Sauce with Laminaria	4,10	0,61	0,99
Sauce with Undaria pinnatifida	3,27	0,60	0,98
Sauce with Fucus	4,14	0,60	0,98

The calculated values of the coefficients of determination (R^2) indicate the high reliability of the analytical equations that describe the behavior of each of the test samples.

According to the decrease in the value of the coefficient of consistency proportional to the viscosity, the test samples can be arranged in the following ranked row: Sauce with Starch → Sauce with Fucus → Sauce with Xanthan gum → Sauce with Laminaria → Sauce with Undaria pinnatifida → Sauce Without thickener. As can be seen from the above data, the properties of the samples at reverse course remain similar to those identified at forward course.

According to the decrease in the value of the rate of destruction of the structure, the test samples can be arranged in the following ranked row: Sauce with Laminaria → Sauce with Undaria pinnatifida → Sauce with Fucus → Sauce Without thickener → Sauce with Xanthan gum → Sauce with Starch. As can be seen from the above data, the properties of the test samples at reverse course have changed compared to the data obtained at forward course. The structure of samples with Laminaria and Undaria pinnatifida is most rapidly destroyed.

The data obtained are shown in Table 4.

Table 4

Thixotropy coefficients (2)

Sample	B_3, **Pa·s**	B_n, **Pa·s**	λ_m, **%**
Sauce with Xanthan gum	4,11	7,22	56,9
Sauce with Starch	6,65	10,39	64,0
Sauce Without thickener	3,22	4,09	84,5
Sauce with Laminaria	4,10	5,00	78,0
Sauce with Undaria pinnatifida	3,27	4,19	82,0
Sauce with Fucus	4,14	7,32	56,6

According to the decrease in the value of the thixotropy coefficient, the test samples can be arranged in the following ranked row: Sauce Without thickener → Sauce with Undaria pinnatifida → Sauce with Laminaria → Sauce with Starch → Sauce with Xanthan gum → Sauce with Fucus. It should be noted that the use of seaweed thickeners instead of traditional thickeners improves the ability of macroscopic systems to self-repair the structure after its destruction.

The obtained results are in complete agreement with the data of parallel studies by IR-spectroscopy to determine the chemical composition of raw materials, sauces and structural changes that occur with raw materials under the influence of technological factors. During these studies, it was found that seaweed raw materials contain amine and hydroxyl polar groups, which under the influence of technological factors interact and form intermolecular hydrogen bonds [37]. These groups of bonds have a positive effect on the structural properties of sauces.

Influence of pasteurization on the viscosity of the developed sauces

In the third series of exams, the effect of pasteurization on the viscosity of the sauces developed was researched. The curves of the dependence of the effective viscosity of the test samples on the shear rate after pasteurization are shown in Figure 3

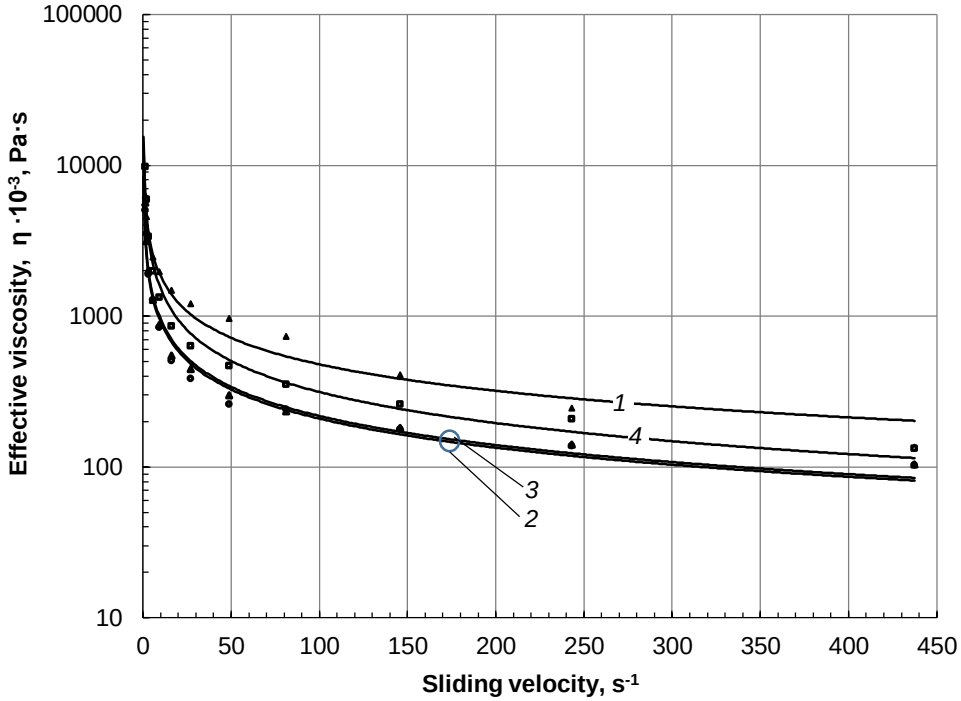

Figure 3. Dependence of the effective viscosity of the samples on the sliding velocity under the influence of pasteurization

1 − Sauce Without thickener, 2 − Sauce with Undaria pinnatifida,
3 − Sauce with Laminaria, 4 − Sauce with Fucus

The results of mathematical processing of the experimental data from Figure 3 are shown in Table 5.

The calculated values of the coefficients of determination (R^2) indicate the high reliability of the analytical equations that describe the behavior of each of the test samples.

Table 5

Effective viscosity of the test samples (η·10^{-3}, Pa·s)

Sample	***B*, Pa·s**	***m***	***R*^{2}**
Sauce Without thickener	7,82	0,59	0,96
Sauce with Undaria pinnatifida	3,99	0,64	0,98
Sauce with Laminaria	4,16	0,64	0,98
Sauce with Fucus	7,32	0,69	0,98

According to the decrease in the value of the coefficient of consistency proportional to the viscosity, the test samples can be arranged in the following ranked row: Sauce with Fucus → Sauce Without thickener → Sauce with Laminaria → Sauce with Undaria pinnatifida.

According to the decrease in the value of the rate of destruction of the structure, the test samples can be arranged in the following ranked row: Sauce with Fucus → Sauce with Undaria pinnatifida → Sauce with Laminaria → Sauce Without thickener. Sample Without thickener is characterized by the lowest rate of structure destruction.

To establish the qualitative and quantitative effect of pasteurization on the viscosity of the test samples, the indicators the coefficient of consistency proportional to the viscosity and the rate of destruction of the structure were summarized in Table 6. The visualization of the analytical data is shown in Figure 4.

Table 6

Influence of pasteurization on the viscosity of the test samples

Sample	B, pa·s			M		
	Before pasteurization	After pasteurization	Change	Before pasteurization	After pasteurization	Change
Sauce Without thickener	10,39	7,82	-2,57	0,56	0,58	0,02
Sauce with Laminaria	4,19	3,99	-0,20	0,64	0,64	0,00
Sauce with Undaria pinnatifida	5,00	4,16	-0,84	0,62	0,64	0,02
Sauce with Fucus	7,32	7,32	0,00	0,68	0,68	0,01

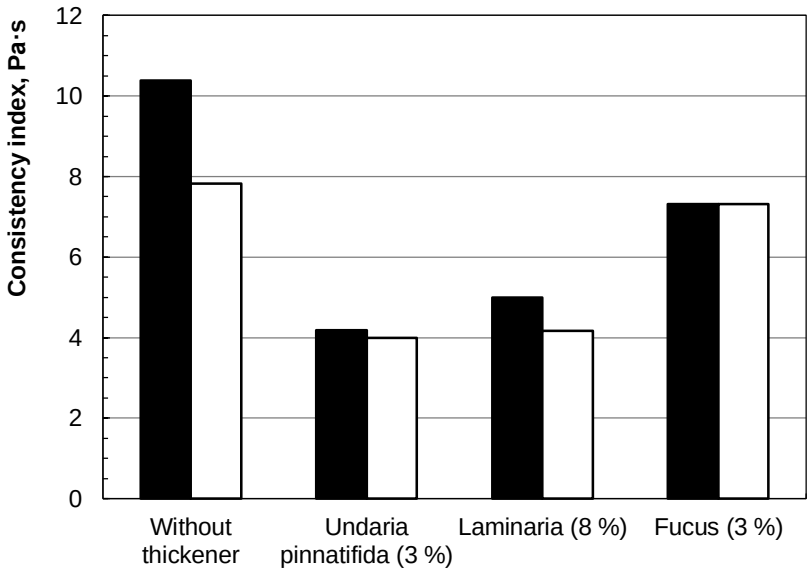

Figure 4. Effect of pasteurization on the coefficient of consistency proportional to the viscosity:
■ – Before pasteurization; □ – After pasteurization

As can be seen from the above data, pasteurization causes a decrease in the consistency ratio of the viscosity for all test specimens except for Fucus sample. At the same time, the largest changes were set for samples without thickener − by 2.57 Pa·s (or by 25%). Samples with Undaria pinnatifida and Laminaria lost 17 and 5%, respectively. No change was observed for the sample with Fucus.

The increase in the values of the rate of destruction of the structure in the range of 1-4% is set for all experimental samples, except for the sample with Undaria pinnatifida. When using Laminaria as a thickener there is an increase of this indicator by 3%, Fucus − by 1%. No change was observed for the sample with Undaria pinnatifida.

The data obtained undoubtedly indicate that the use of seaweed as thickeners improves the structural properties of pasteurized objects of research. These changes can be explained by structural changes that occur with alginates under the action of elevated temperatures [38].

Conclusions

1. Samples of sauces, made by the developed technology without the addition of special structure-forming agents, have rheological dependencies, similar to analog samples, made with the addition of the most common structure-forming agents.
2. The use of some seaweed may increase the viscosity of the target products compared to the control samples
3. The use of seaweed thickeners instead of Xanthan gum improves the ability of macroscopic systems to self-repair the structure after its destruction.
4. The use of seaweed as thickeners improves the structural properties of pasteurized objects of research.
5. The possibility of producing berry sauces with iodine-containing additives without the addition of structure-forming agents to the formulation was proved.

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Efficiency of gas chromatographic analysis of terpens and terpenoids of sources of aromatic substances, taking into account the polarity of the stationary phase

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Abstract

Introduction. The aim of the study is to increase the efficiency of gas chromatographic analysis of terpenes and terpenoids based on the polarity of the stationary phase.

Materials and methods. It is used a model matrix №1 from a mixture of terpenes and a model matrix №2 from a mixture of terpenoids, obtained by preparative isolation in individual composition with confirmation of purity of isolation by Kovach index (IK). The analysis was performed on a chromatograph GC 8000 series, carrier gas – helium, detector – flame ionization (FID). The criteria for selecting SP GC analysis according to the Rorschneider polarity system were used.

Results and discussion. The separation of terpenoids (polar AS) into non-polar SP, the bonds inherent in polar molecules (dipole or hydrogen bonds) do not occur, so terpenoids are kept on non-polar SP SE-30 much weaker than on polar SP Carbowax 20M. The higher the values of R_s, the more efficient the gas chromatographic system of separation of terpenoids. For the column with SP Carbowax 20M R_s = 1.67, for the column with SP SE-30 R_s = 1.16.

The quantitative characterization of the universality of the studied SP with respect to the separation of terpenoids by polarity is the difference of the Kovach GIC indices. So for linalool on SP SE-30 – IR=1093, for Carbowax20M – IR = 1582. This means that less polar terpenoids will leave the gas chromatographic column earlier for more polar AS while ensuring complete separation of the complex mixture and the possibility of reliable and reproducible installation component composition of the prototype.

The retention time of terpenes increases with decreasing polarity of SP. Of the two experimental SP, the nonpolar SP SE-30 has a greater affinity for terpenes of the model matrix №1, which precludes obtaining on chromatograms of unresolved peaks for a critical pair of components with close T_{boil}. The calculated values according to the Rorschneider polarity system indicate the different polarity of the studied SP and the manifestation of characteristic intermolecular forces. When separating critical pairs of terpene hydrocarbons with close Tboil (α-terpinene 172.5 ºC, d-limonene 173 ºC, α-phellandrene 172 ºC) on a non-polar stationary phase (SE-30=4.40) the yield of components from the column is separated. peak. The use of a low-polar stationary phase (HP-5ms, R_p> 15) provides a consistent output of critical pairs of terpene hydrocarbons by individual peaks in T_{boil}.

Conclusion. The results of the research allow us to increase the reproducibility of gas chromatographic analysis of sources of aromatic substances, as well as to choose SP, which can be interchangeable and provide a similar separation.

Introduction

There is still no single system theory that comprehensively describes the chromatographic process. With the development of GC analysis in the world, basic theories of separation of complex mixtures of natural and synthetic origin were developed [1–7], as well as practical aspects of the implementation of theoretical developments [8, 9].

A multifaceted task is to conduct an effective GC analysis of sources of aromatic substances. Low reproducibility of the results of such studies, especially in interlaboratory determinations, is a problem widely discussed among chromatographers [10, 11]. Therefore, a significant part of scientific works is devoted to the search for theoretical and practical ways of developing the gas chromatographic method to increase the probability of the obtained results of the analysis of sources of aromatic substances, reducing their differences [11–13].

Scientific publications on GC analysis of sources of aromatic substances are concentrated in specialized journals [14, 15]. Food flavor studies are less represented. This analysis is complicated by the instability of the component composition of sources of aromatic substances in food, which is influenced by the location and seasonality of raw materials, varietal affiliation, method of processing [16–18].

The reason for the differences in the results is not only due to insufficient elaboration of the theory of intermolecular interactions between terpenes, terpenoids in terms of their contact with SP of different polarity [17,19]. The analysis is complicated by the presence in natural sources of the aroma of substances of different homologous series, including terpenes, oxygen-containing components, which are separated in a narrow range of boiling points (T_{boil}). This causes overlapping and masking of peaks on the chromatograms of different sources of AS. [11, 12, 20].

Indeed, in GC analysis of sources of aromatic substances, the balanced distribution of components in the column is established over time. Therefore, the concentration zones during the migration of components along the column can expand, "blur". This complicates the accurate determination of the qualitative composition and quantitative content of the components of aromatic substances in food and requires the correct choice not only of the modes of GC analysis, but also SP analytical column.

It is known that the correct choice of the stationary phase (SP) of the analytical column [21] largely depends on the efficiency of GC analysis.

The methodology of SP evaluation according to different selection criteria is considered in many classical works [22-25], in modern publications [1, 21, 26]. In turn, M. Wigderhaus proposed to divide SP into 7 main groups based on the relationships between the constants of the Rorschneider system and the McReynolds scale [27] with the participation of the chromatographic polarity Pp, [1, 16, 22, 28].

Rorschneider [29] proposed a formula that calculates the relative chromatographic polarity of PS – Ps, % and compiled a system of polarity of SP, in particular: nonpolar (Ps = 0 – 5%), weakly polar (Ps = 5 – 15%), medium polar = 15 – 35%), strongly polar (Ps = 50 – 100%). McReynolds proposed the SP selectivity scale as a development of the Rorschneider system [30]. According to this scale, the selectivity of SP is estimated as the difference between the content indices of Kovach GIC 10 standard substances with close Tboil. In addition to benzene (X), butanol (B), methyl propyl ketone (Z), nitropropane (U), pyridine (S) proposed by Rorschneider [29, 30], 2-methyl-pentanol-2 (H), 1-iodobutane (I), octin-2 (K), 1,4-dioxane (L), cis-hydrindane (M). The higher the values of the McReynolds constants, the greater the selectivity of SP to the components of the mixture with close to boiling point T, the longer they will be in contact with SP. Components with low values of McReynolds constants will come out of the column first.

At the same time, it should be noted that the criteria for the selection of effective SP developed by scientists so far are being criticized and work is underway to find new approaches that can be reproduced in different laboratories [10, 31].

The relevance of such research is based not only on purely scientific or cognitive interest. We are talking about the requirements of the rapidly growing worldwide industry of food flavors and synthetic flavors [32, 33].

The study aims to study the effectiveness of gas chromatographic analysis of terpenes and terpenoids taking into account the polarity of the stationary phase and the formation of criteria for selecting SP for the analysis of aroma sources according to the Rorschneider polarity system.

Materials and methods

Materials

Two model matrices are used in the work.

Model matrix №1. The model matrix №1 included 7 terpene hydrocarbons (terpenes) of individual composition isolated by laboratory preparative chromatography. These are: α-pinene, camphene, β-pinene, β-myrcene, β-phellandrene, α-terpinene and d-limonene.

In the Table 1 information on the characteristics of the model matrix №1 is collected.

Model matrix №2. The model matrix №2 combines oxygen-containing components (terpenoids) of different chemical classes of aliphatic and cyclic nature, in particular alcohols (aliphatic l-linalool, monocyclic α-terpineol), aldehyde (citral), ketone (carvone), ester of terpene and terpene acids (geranyl acetat).

In the Table 2 information on the components of the model matrix №2 is collected.

Research methods

Preparative chromatography for laboratory production of terpenes, terpenoids of individual composition from cumin essential oil

Obtaining terpene hydrocarbons was controlled distillation of cumin essential oils into fractions at stage 1 in the adiabatic mode according to technological maps [34] with their subsequent concentration in "narrow fractions" with a component content 65–75% of the mass. Preparative chromatography (stage 2) was used to disperse the "narrow fractions" into terpenes and terpenoids. An effective nozzle of the preparative column with a gradient application of portions of the stationary phase PEG6000 on individual sections of the solid carrier (Chromosorb A) was developed. Table 3 shows the sequence of application of SP on TN.

Modes of preparative isolation of terpenes, terpenoids of individual composition: preparative chromatograph "Chromium 31A". Column dimensions: steel spiral tube 500x10 mm (inner diameter). Solid carrier: Chromosorb A (30/40 mesh). Smobile phase Polyethylene glycol adipinate – PEG-6000. Application of NF on TH – gradient Temperature: injector (180– 250) °C, column thermostat (145–210) °C (with clarification for each fraction). Carrier gas: nitrogen 1.33 m^3/h. Column load: 0.6±0.1 to 1 g (for repeated cycles). Detector: 170 mA catharometer [35].

Table 1

Generalized characteristics of the model matrix № 1

Component matrix	Method of obtaining	Ps**	T_{boil} , °C
1. β-myrcene	PS *, mass spectrum	+4	167±2,0
2. β-phellandrene	PS *, Kovach index	+3	172±2,0
3. d-limonene	PS *, Kovach index	+3	172±2,0
4. Kamfen	PS *, Kovach index	+2	159±2,0
5. β-pinene	PS*, mass spectrum,	+2	160±2,0
6. α-pinene	PS *, Kovach index	+1	153±2,0
7. α-terpinene	PS *, Kovach index	+1	173

* PS – preparative selection, ** polarity

Table 2

Generalized characteristics of the model matrix № 2

Component		Method of obtaining, identification	Tboil °C	Ps**
1	citral	PS *, Kovach index	176,0±2,0	+3
2	d- carvone	PS *, optical activity	230,0±2,0	+3
3	l-linalool	PS *, optical activity	198,0±2,0	+4
4	geranyl acetate	PS *, mass spectrum,	199,0±2,0	+3
5	ά-terpineol	PS *, mass spectrum,	224,0±2,0	+3

* PS – preparative selection, ** polarity

Table 3

Sequence of application of SP on TN preparative column

Number section	Particle size, mm	Content, % mass	Column filling volume, g	Weight, g
1	2,0–3,0	15	97	48,00
2	1,0–2,0	25	148	70,87
3	0,56 –1,0	60	240	130,00

Determination of the Kovach index

Kovach index is calculated according the method based on the recorded gas chromatographic characteristics [36].

Identification of conformity of substances of preparative allocation to a chemical class of terpenes, terpenoids

Identification was performed according to the Kovach index [36].

Identification of conformity of substances of preparative selection to the chemical class of terpenes, terpenoids by mass spectra

The LECO/Fiehn Metabolomics Library and the 2011 Pfleger-Maurer-Weber Mass Spectrum Database (approximately 8,500 compounds) were used for identification. The results were processed by the data processing system of the MX-E model. The identity of both mass spectra ≥92% confirms the identity of the component with a probability of more than 92%.

Modes of GC analysis of test samples

The analysis was performed on a GC 8000 series chromatograph, carrier gas – helium, costs: through the column – 1 cm^3/min, through the column – 1.2 cm^3/min, for discharge from the injector – 100 cm^3/min, programming the temperature of the column thermostat: initial – 100 ºC, final – 180 ºC; programming speed – 8 ºC/min; sample volume 0.2 µl. Detector – flame ionization (FID).

Removal of chromatographic profiles

The areas of the chromatographic peaks of the As model matrix were calculated by the electronic automated system CAA-006 by the method of internal normalization with statistical processing of data from parallel experiments (5 repetitions). The variance of the deviation S2 was calculated, the reliable interval of probable values±σ relative to the critical Student's criterion Tcr = 4.42.

Establishing the level of the polarity of the components of the model matrix

Table 4 show systematization of AS on the manifestation of hydrogen bonds the sequence of application of SP on TN.

Table 4

Systematization of AS on the manifestation of hydrogen bonds the sequence of application of SP on TN

Class characteristics	Aromatic substances	Polarity
Class 1. Repeated manifestation of hydrogen bonds	Polyphenols	+5
	Hydroxy acids	
Class II. The presence of both a donor atom (O, N) and an active hydrogen atom	Alcohols, geraniol, nerol, citronellol, farnesidol, terpineol, menthol, borneol	+4
	Phenols: eugenol	
Class III. The presence of a donor atom, the absence of an active hydrogen atom	Ethers	+3
	Citral, gerenial, citronenal, carvone, camphor	
	Esters – geranyl acetate, linalyl acetate	
Class IV. The presence of an active hydrogen atom, the absence of a donor atom.	Unsaturated hydrocarbons – limonene, α, β-pinene, camphene	+2
	Terpene, sesquiterpene, aromatic hydrocarbons	
Class V. Do not form hydrogen bonds	Saturated hydrocarbons	+1

The systematization of AS on the manifestation of hydrogen bonds [36-38], the ability to form a dipole, and orientation interactions (Table 5), [30].

Table 5

Systematization of AS by the ability to form dipole and orientation interactions

Class characteristics	Aromatic substances	Polarity
Molecules without permanent dipoles or functional groups	-	+1
Molecules with almost imperceptible dipoles	Terpenes, sesquiterpenes	+2
Molecules with constant dipoles, electronegative atoms, but without a single active hydrogen atom	Aromatic alcohols, aldehydes, terpene ketones, esters, lactones and acids	+3
Molecules with strong dipole moment, free electron pairs	Aliphatic, terpene and sesquiterpene alcohols, phenols and phenol esters	+4
Molecules with a strong dipole moment and a three-dimensional arrangement of hydrogen bonds	-	+5

Establishing the polarity of SP effective against AS sources of aroma by the values of Rorschneider constants

Reference tables with values of SP polarity according to the Rorschneider system were used [27] and the selected SP are effective against AS sources of aroma.

According to the Rorschneider polarity system, the value of the relative polarity P_P is calculated by the following formula

$$P_p = \frac{(x + y + z + u + s)}{5 \cdot 10} \quad (1)$$

x, y, z, u, s are Rorschneider constants

In formula 1, the Rorschneider constant x characterizes mainly inductive interactions. Rorschneider's constant y- is mainly donor-acceptor interactions of terpene alcohols.

The Rorschneider constant z is responsible for dipole-dipole (orientation) interactions of ketones, aldehydes, ethers, esters. The Rorschneider constant u is mainly related to the hydrogen bond of cycloaliphatic compounds. The Rorschneider constant s is related to orientational interactions. These are AR complex compounds, including oxygen-containing substances, macrocyclic lactones, and oxylactones.

According to Rorschneider, nonpolar SP include those for which P_p= 0–5, weakly polar P_p = 5–15, medium polar – P_p = 15–35, strongly polar – P_p = 50–100.

Determination of characteristic indicators of GC analysis [27].

The degree of separation of RS, as the ability of the GC column to separate the "critical pair" of components (d-carvone and citral). The following formula was used:

$$R_s = \frac{2 \cdot (t_{R2} - t_{R1})}{w1 + w2}$$

where: t_{R2}, t_{R1} – retention time, min, w1, w2 – peak width of d-carvone and citral along the zero line, mm.

The selectivity of the separation α was calculated by the following formula:

$$\alpha = \frac{t_{R1}}{t_{R1}}$$

where: t_{R2}, t_{R1} – retention time of the first and last components at the exit of the column. In practice, GC analysis is considered satisfactory value of ά within 0.8– 1.0

The extraction coefficient k' was found as the ratio of the corrected retention time t′R – to the "dead time" t_0:

$$k' = \frac{t_R}{t_{R0}} = \frac{t_{R2} - t_0}{t_0}$$

Results and discussion

Investigation of the efficiency of gas chromatographic analysis of terpenoids taking into account the polarity of the stationary phase

Table 6 shows the results of the study of the effectiveness of the influence of intermolecular interactions of terpenoids of the model matrix № 2 and SP of different polarities. The studies calculated the logarithm of the relative retention time of lgt′R on chromatograms obtained on capillary columns with non-polar SP SE-30 and polar SP Carbowax 20M.

Table 6

Signals of terpenoid content on SP of different polarity

Terpenoids	**Stationary phases**					
	SE-30 (a)			**Carbowax 20M (b)**		
	lgt'_R		IK_a*	lgt'_R		$IK_в$
Linalool	2,32		1093	2,81		1582
α-terpineol	2,72		1230	2,92		1591
Citral	2,87	**Rs =1,16**	1272	3,42	**Rs =1,67**	1767
d-carvone	2,83		1264	3,01		1725
Linalyl acetate	2,92		1290	3,47		1783
Geranyl acetate	3,08		1308	3,64		1848

* Estimated values of Kovach indices (IK).

Based on the data in Table 6, the following provisions should be discussed.

Terpenoids with different functional groups belong to polar compounds, so they last longer on polar SP than on non-polar SP.

Terpene alcohols have sp3-hybridization of the oxygen atom of the hydroxyl group [27]. This determines their electron-donor properties. The polar bond (C – O) and (O – H) are capable of forming hydrogen bonds. Unlike terpene alcohols, aldehyde and ketone molecules do not have mobile hydrogen atoms that are bound to oxygen atoms. As a result, the aldehyde citral and ketone d-carvone are less reactive than alcohols but show orientational interactions.

This affects the fact that in polar SP terpene alcohols are obtained earlier than aldehydes.

Geranyl acetate ester has the longest retention time among the terpenoids studied and shows better separation into polar SP. In such interactions, the orientation forces are shown mainly. Modification of nonpolar SP by strongly polar AS can also occur with the formation of instantaneous dipole moments of induction interactions.

The difference in relative polarity in the group of terpenoids is also explained by the difference in their structural structure. Thus, the most polar of the studied terpenoids are geranyl acetate (Table 2). It has the longest retention time on the column with SP Carbowax 20M.

The interaction of SP SE-30 with terpenoids is determined mainly by dispersion forces. Therefore, terpene alcohols on a non-polar column have a significantly shorter retention time (lgt′R) compared to SP Carbowax20M (linalool 2.32, 2.81).

Indicative, when comparing gas chromatographic columns, is the value of Rs. Under the condition Rs <1, the peaks overlap. Accurate determination of parameters, especially quantitative ones, becomes impossible [23]. Therefore, the higher the values of Rs, the more efficient the gas chromatographic system of separation of terpenoids.

From the Table 6 we observe the difference of Rs values for the studied columns. For the column with SP Carbowax 20M Rs = 1.67, for the column with SP SE-30 Rs = 1.16.

The difference of Kovach ΔIK indices can also be considered as a quantitative characteristic of the universality of the studied SP (a, c) in terms of the separation of terpenoids by polarity.

$$\Delta IK = \left| IK_в - IK_a \right| \quad (2)$$

A higher value for the ΔIK of the test substance on one of the compared SP indicates a higher polarity of this SP, and this As behaves on this SP as a more polar substance.

According to the obtained data (Table 6) for linalool on SP SE-30, IR = 1093, for Carbowax20M, IR = 1582. This means that of the compared SP polarity Carbowax20M is much greater than in SP SE-30.

Studies have shown that less polar terpenoids will leave the gas chromatography column earlier than more polar AS. Therefore, Carbowax 20M shows greater polarity than SP SE-30.

Investigation of the efficiency of gas chromatographic analysis of terpenes and taking into account the polarity of the stationary phase

Studies of the separation of the model matrix, 2, which consisted of terpenes on columns with nonpolar SP SE-30 and polar SP Carbowax 20M (Figure 1).

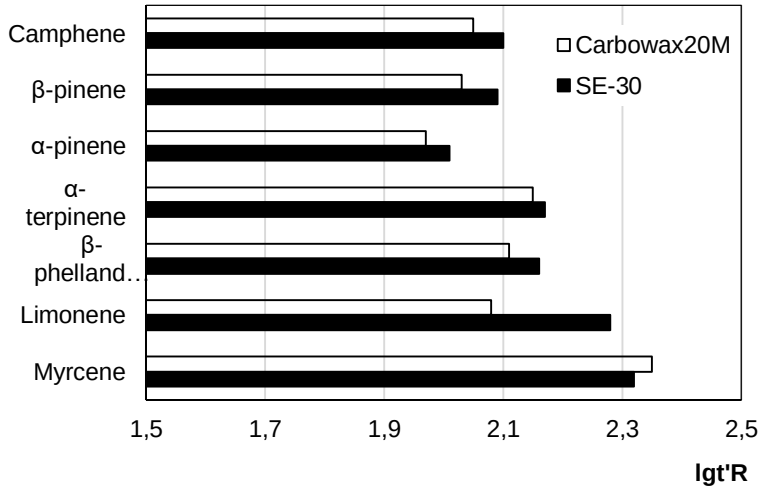

Figure 1. lgt'R AR terpenes obtained on SP of different polarity

Chromatograms were calculated relative to the logarithm of the corrected retention time – lgt'R components of the model matrix taking into account the time of methane yield (t_m = 44 s).

Based on the data in Figure 1, the following provisions should be discussed

The results show noticeable differences in the interaction of nonpolar terpenes with SP of the corresponding and opposite polarity. The diagram shows that the components with a cyclic structure (camphene, α- and β-pinene) have a lower retention time than substances of aliphatic structure (myrcene) on both SP. The increase in the number of cycles in the structure of the molecule reduces the retention time of the components. The presence of double bonds increases the polarity of the components. Thus, monocyclic α-terpinene with two double bonds in the middle of the ring (Figure 1) interacts equally with SP of different polarity. The appreciable difference of the maintenance of d-limonene on SP of various polarity is explained by the existence of double communication outside of a ring. In our opinion, limonene has the strongest bond with SP Carbowax 20M due to the proximity of the natural chemical structure. Myrzen with three double bonds is the most polar of the other terpenes. This explains its longer retention time in polar SP. In addition, there is a partial deformation of SP Carbowax 20M under the influence of the induced dipole moment.

It should be noted that the double bond in the middle of the α-pinene cycle affects the reduction of retention time on both SP in comparison with β-pinene, in which the double bond is in the side chain of the cycle. Also, β-myrcene, d-limonene, camphene, β-pinene have a pair of π-bonds in the extreme chain and are fundamentally more polar than terpenes with double bonds in the middle of the ring – α-pinene, β-felladndren, α – the patient.

Therefore, the retention time of terpenes increases with decreasing polarity of SP. Of the two experimental SP, nonpolar SP SE-30 has a greater affinity with terpenes of the model matrix №1, extends the ability to avoid undivided peaks for components with close T_{boil}.

Selection of effective SP GC analysis of aroma sources according to the Rorschneider system taking into account the chromatographic polarity of P_P.

The study was performed with the participation of two nonpolar SP – SP -SE-30 and SP-HP-5ms.

The values of P_P for the studied SP were calculated by the difference of the Kovach indices (IK) according to the following formula:

$$P_p = \frac{\Delta IK_x + \Delta IK_y + \Delta IK_z + \Delta IK_u + \Delta IK_S}{5 \cdot 10} \quad (3)$$

where: ΔIKx characterizes mainly induction interactions and shows the degree of increase in terpene retention time.

ΔIKy- mainly donor-acceptor interactions of terpene alcohols.

ΔIKz is responsible for dipole-dipole (orientation) interactions of ketones, aldehydes, ethers.

ΔIKu is mainly associated with the hydrogen bond of cycloaliphatic compounds.

ΔIKs is associated with the orientational interactions of oxygen-containing substances, macrocyclic lactones and oxylactones.

The results of the determination of IK terpenes on nonpolar SP-SE-30 and SP -HP-5ms are shown in the Table. 8.

Table 8

Values of hydrocarbon (IK) content of terpenes for the studied SP

Terpenes	SP – SE-30			SP – HP-5ms		
	lgV'_R	lgt'_R	IK	lgV'_R	lgt'_R	IK
α-pinene	2,00	2,00	942	2,00	2,00	1039
camphene	1,20	2,07	951	1,28	2,11	1083
β-pinene	1,48	2,17	968	1,58	2,19	1124
α-terpinene	1,89	2,24	1010	2,09	2,33	1190
d-limonene	2,04	2,31	1021	2,29	2,36	1206
β-phellandrene	2,24	2,36	1025	2,16	2,39	1216

In the Table 7 there is shown the values of the Rorschneider constants and calculates the polarity of the studied SP.

Table 7

Polarity P_P of the studied SP according to the Rorschneider system

Names SP	**Rorschneider's constants**					$\sum \Delta IK_{1-5}$	P_p
	ΔIK_1 (x)	ΔIK_2 (y)	ΔIK_3 (z)	ΔIK_4 (u)	ΔIK_5 (s)		
SE-30	16	53	44	64	41	220	4,40
HP-5ms	52	172	95	198	147	734	15,36
Carbowax 20M	322	536	368	572	510	2308	46,15

The calculated values Pp indicate the different polarity of the studied SP and the manifestation of characteristic intermolecular forces. Terpene hydrocarbons are more characterized by dispersion interactions (90– 95%) and instantaneous induction interactions (5 ¼ 10%).

The obtained data allow to select SP which can be interchangeable, ie to provide similar division.

In Figure 2 there is shown the chromatograms of the model matrix № 1 obtained on capillary columns with nonpolar SP SE-30 (P_p = 4.40) and weakly polar SP HP-5ms (P_p = 15.36). The obtained chromatograms revealed differences in the separation of terpenes of the model matrix into SP of different polarity.

Analysis of the chromatograms showed that the column with SP SE-30 showed incomplete separation of critical pairs of terpenes (groups 1 and 2). The calculated molecular statistics for the critical pair of camphene and β-pinene (1) on SP SE-30 have a selectivity coefficient α1 = 0.67; extraction factor k_1'= 1.22; separation criterion R_{S1}= 0.91. For the pair β-phellandrene and α-terpinene (2): α2 = 0.78; k_2'= 1.26; R_{S2}= 0.94. On the column HP-5ms for pair 1: α1 = 1.32; k_1'= 3.12; R_{S1}= 1.56. For pair 2: α2 = 2.75; k_2'= 3.86; R_{S2}= 2.04.

In addition, the column with SP HP-5ms shows a prolonged retention time of terpenes. The camphene is the most polar component of the matrix and lasts longer on SP HP-5ms than on SP SE-30.

Such data allowed to propose a working column with SP HP-5ms for GC analysis of terpene hydrocarbons (Table 8).

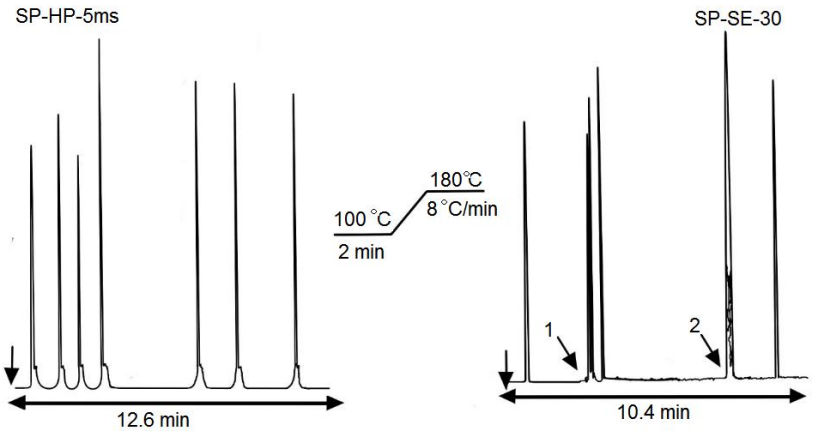

Figure 2. Chromatograms of the model matrix obtained on capillary columns with SP – SP SE-30 and HP-5ms

Table 8

Characteristics of the capillary column HP-5ms

Indicator	Value
Column material	quartz
Stationary phase	HP-5ms, (DB-5 ms)
Operating temperature, ° C	320
Geometric dimensions (d/L)	30 м/0,25 мм
The thickness of the SP film, μm	10
Rorschneider polarity	15,36
Number of theoretical plates	21162–22071
Height of the theoretical plate (VETT), mm	0,7–0,94
Column selectivity for b-pinene and β-terpinene	1,42; 1,8.
Calculated extraction factor	k' = 1,32–1,64

Note that due to the close Tboil critical pairs of terpene hydrocarbons with the imposition of peaks, there is a need to correct the conditions of gas chromatographic analysis.

Conclusions

Studies have shown the need to take into account the polarity of P_P SP column when GC analysis of terpenes and terpenoids of the experimental mixture of aromatic substances. This indicator is directly related to the energy of intermolecular interactions of AS with SP, and affects their retention time in the column, Kovach index, value Rs as an indicator of the purity of the separation.

It was found that when separating terpenoids (polar AS) into nonpolar SP bonds inherent in polar molecules (dipole or hydrogen bonds) do not occur, so terpenoids are retained on nonpolar SP SE-30 much weaker than on polar SP Carbowax20M . Under such conditions, less polar terpenoids will leave the gas chromatographic column earlier than more polar AS ones.

The retention time of terpenes increases with decreasing polarity of SP. Of the two experimental SP, nonpolar SP SE-30 has a greater affinity with terpenes of the model matrix №1, excludes obtaining on chromatograms of unresolved peaks for components with close Tboil.

Therefore, taking into account the polarity of the stationary phase, the efficiency of gas chromatographic analysis of terpenes and terpenoids increases due to the maximum exclusion of overlap and masking of peaks on chromatograms, obtaining the most separated front of the mixture components and accurate determination of qualitative composition and quantitative content of components

The results of research allow us to increase the reproducibility of gas chromatographic analysis, as well as to choose stationary phases that can be interchangeable and provide a similar separation, which will reduce the cost of the laboratory budget.

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Improvement of the operation processes of electrotechnology wastewater treatment systems under the energy efficiency criterion

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Abstract

Introduction. The research is conducted to justify of substantiating scientific foundations for the functioning of electrotechnological wastewater treatment systems of continuous production.

Materials and methods. The approaches towards the creation of technical specifications for continuous production are being analyzed, taking into consideration the criteria of energy efficiency. The study is based on the methods of active and passive experiments on pilot plants and industrial equipment, the methods of cross-effects of water purification methods, the methods of the dominant dynamic pollutant, the modeling concept based on the notations of the universal modeling language UML for efficient processing of measurement information.

Results and discussion. The architecture of the control system with adaptive adjustment of control strategies in real time is substantiated. The system makes it possible to make decisions under conditions of disturbances of natural and man-made origin, taking into account the criterion of energy efficiency. The generalized system includes: a local control system and a decision subsystem with an input signal filtering unit (the decision subsystem contains a block for adaptive formation of control strategies in real time based on Kohonen self-organizing maps). Practically implemented approaches to the object-oriented creation and implementation of technological regulations for combined electrotechnological systems for wastewater purification of continuous production. This made it possible to improve the energy efficiency of multicomponent effluent purification processes for a meat processing enterprise deviating the energy efficiency criterion from zero ± 9.6 %, and small metallurgy ± 3.4 %. The synthesis method of object-oriented technological regulations was further developed to improve the control algorithms for combined electrotechnological water purification systems of continuous production based on the energy efficiency criterion, based on assessing the efficiency of using energy resources as an integral parameter for the removal of pollutants from effluents. Intelligent energy-efficient control of the process of removing the contaminants from wastewater is being realized through the synthesis of software and information control of the combined electrotechnology wastewater purification systems based on the object-oriented technical specifications for operation.

Conclusion. An improved method for managing the operation of electrotechnological wastewater treatment systems for continuous production ensures compliance with the requirements for the efficient use of energy resources and environmental safety.

Introduction

The use of technical and technological solutions to ensure the processes of wastewater treatment are to provide peculiar valid technological modes for the operation of such systems and meet the requirements of environmental safety and quality of wastewater purification [1, 2]. Establishing a relationship between energy consumption levels and the quality of wastewater treatment appears to be an individual task in the formation of the resource allocation for the operation of the industrial wastewater purification systems.

Increased efficiency is achieved by improving the technological regulations for the appropriate complex of equipment for wastewater purification based on the current water passport of the enterprise [3]. The sequence of creating the requirements documents, as universal decisions, is to be based on permanent, temporary, non-recurrent technical specifications (TS) as well as the peculiarities of operation of the specific equipment, which is currently installed at the enterprises.

Wastewater differs from each other in the type and concentration of pollution, the rate of entry and other factors. Based on the multicomponent nature of wastewater, the following basic methods of wastewater purification exist [3–6]: mechanical (physical) methods, chemical methods, physical and chemical methods, biological methods, combined methods. However, the common drawbacks of such methods is that it is necessary to monitor dozens of parameters of water quality and technological processes in real time.

Only industrial units of automated measuring instruments exist and operate reliably at continuous production [7, 8]: temperature, pressure, turbidity, flow rates, pH, redox potential, biological oxygen consumption, chemical oxygen consumption, absorption of chlorine, ionic composition. Other studies can only be carried out in laboratory conditions – these include express methods, since there is still a time delay from sampling to transmitting information to technological equipment. Moreover, when designing water purification systems, the possibility of emergency situations of industrial and natural origin is not taken into account, which is necessary for efficient and rational nature management [9]. The task of creating complex criterion for evaluating the performance of systems remove contaminants from aqueous solutions and energy costs for its implementation was not solved by any of the researchers.

Moreover, all the described modern methods of removing pollutants from wastewater require the use of electrical systems (in which the conversion of electrical energy to other types of energy with the simultaneous implementation of technological processes) [10]. There are effective methods of water purification, however, due to the lack of the necessary list of measuring complexes, they work either environmentally dangerous or with the re-deployment of resources.

There are a large number of publication devoted to the design and study of mathematical models of electrode [15] and electro-membrane systems for removing pollutants from aqueous solutions [16]. An analytical study of wastewater purification from organic pollution in bioreactors-aerotanks with suspended and fixed biocenosis was carried out, which made it possible to optimize the work of biological water purification methods [17]. Separately, the direction of creating mathematical models of technological equipment is highlighted, which in the future will be the basis of automated control systems [18, 19]. Each of the options for modeling water purification processes has both advantages and disadvantages [20, 21]. But only a combination of physical and mathematical modeling of the processes of removing pollutants from aqueous solutions and the theory of automatic control in a single scientific method will allow integrating the strengths of the approaches and minimizing weaknesses.

That is why improving approaches to the creation and functioning of electrotechnological wastewater purification systems and reducing their total energy consumption is an urgent scientific and practical task [11]. This situation is also stimulated by the fact that drainage and water purification systems are developing at a rapid pace (an annual increase in their productivity of 4–5 %) [12, 13].

The research is conducted to justify of substantiating and creating scientific foundations for the functioning of electrotechnological wastewater purification systems of continuous production, the functioning of which will meet the requirements of the efficient use of energy resources and environmental safety.

Materials and methods

Materials

The object of research is electrotechnological wastewater purification systems for continuous production on the example of a meat processing enterprise and a minor metallurgy enterprise.

For the achievement of the put aim the work uses the methods of active and passive experiments on pilot plants and industrial equipment, the methods of cross-effects of water purification methods, the methods of the dominant dynamic pollutant, the modeling concept based on the notations of the universal modeling language UML for efficient processing of measurement information. The modern approaches towards the creation of technical specifications for continuous production are being analyzed, taking into consideration the criteria of energy efficiency.

Methods

Research plan

The research includes stages:

- Substantiation of the improvement of methods for creating technological regulations for wastewater purification systems based on the criterion of energy efficiency;
- Substantiation of methods for improving the functioning of electrotechnological wastewater purification systems based on effective processing of measurement information;
- Development of a model of a water purification process control system when processing measurement information in real time;
- Experimental study of the created control system for electrotechnological water purification at a meat processing plant;
- Analysis of the research results of electrotechnological water purification systems for continuous production for compliance with the requirements for the efficient use of energy resources.

Methods for creating technological regulations for wastewater purification systems

Improvement of the TS for the combined electrotechnology wastewater purification of the continuous production is based on the use of familiar basic methods [21, 22], taking into account the technological scheme and elimination modes for the potential natural and man-caused emergency situations, nomenclature and operation modes for wastewater purification equipment on the basis of complex acknowledgement of investments efficiency and energy efficiency levels in particular (Figure 1).

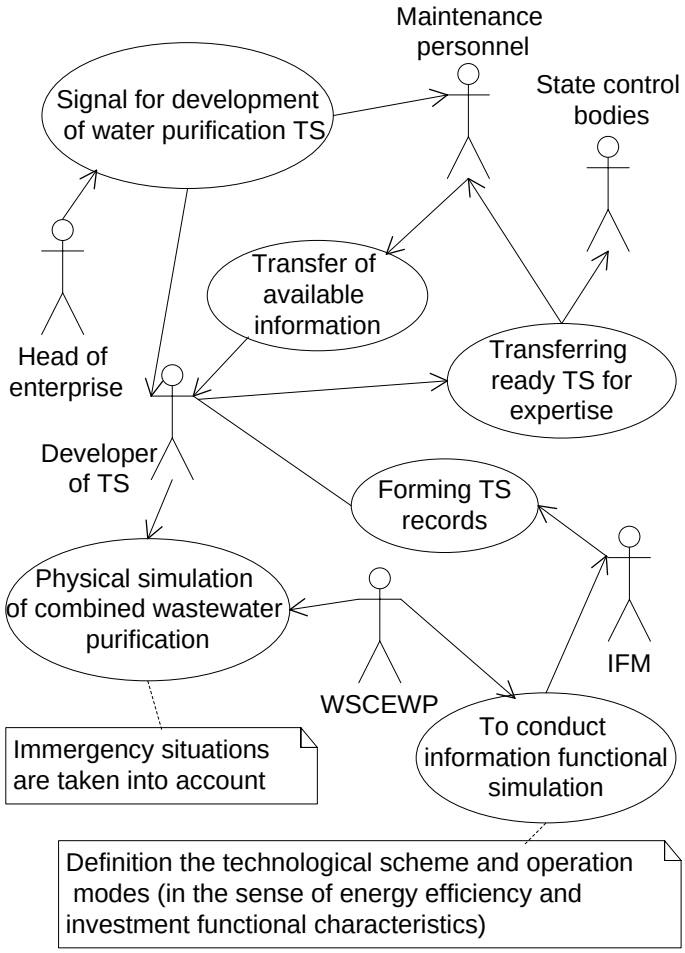

Figure 1. The building and logical scheme for the creation of the TS for the combined electrotechnology wastewater purification of the continuous production (UML notes)

Method of improving the functioning of electrotechnological wastewater purification systems based on effective processing of measurement information

Stages of modeling the impact of emergency situations when setting up equipment for wastewater purification [1, 9, 11]:

- When creating model solutions before treating water with the use of working standard of the combined electrotechnology wastewater purification by adding the contaminants with exceeding values which are recorded in the water passport of a particular enterprise;
- When forming the knowledge base for the synthesis of the simulation modeling neural network.

The object-oriented logical sequence of the advanced TS synthesis method includes a number of steps (Figure 2) [1, 11].

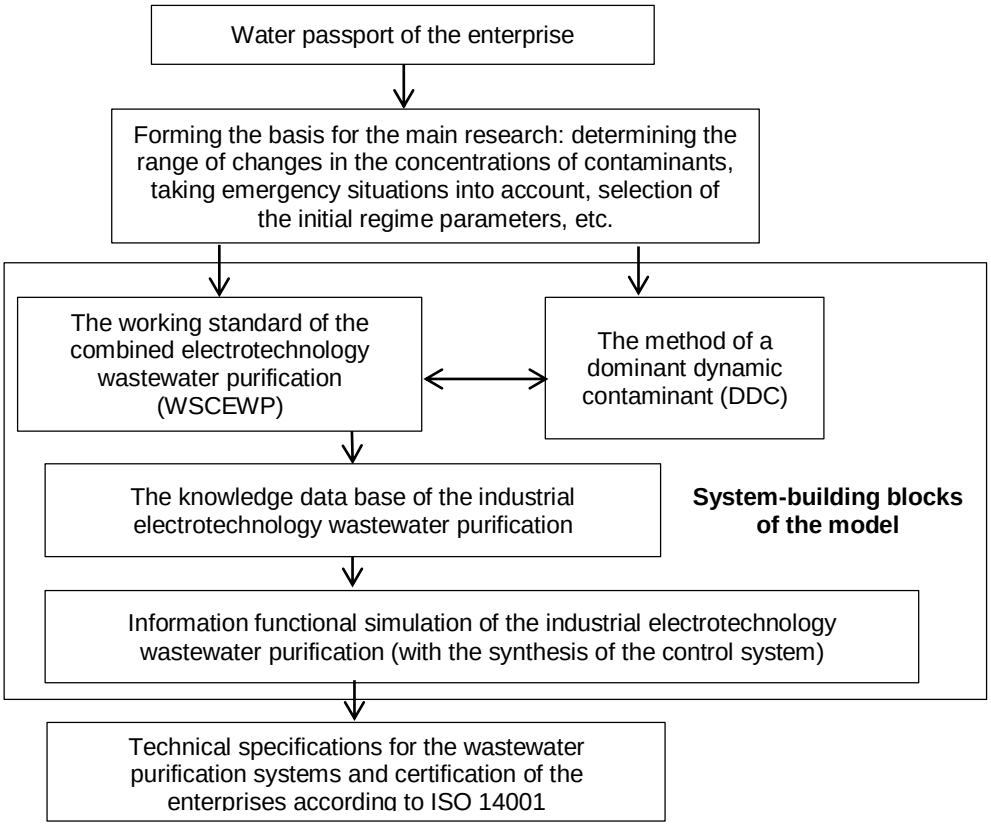

Figure 2. Logical model of the TS synthesis on the basis of an effective obtaining and processing of measurement information taking into account the effect of emergency situations

Cross-effect of different water purification methods

An analysis of the operation of purification systems, in the case of a combination of basic methods [24], showed the superposition of the action of different equipment on the same pollutants. On the basis of the results obtained, the sequence of creation of water purification systems with the expansion of functional capabilities and their ability to effectively counteract emergency situations is justified – the cross-effect of methods for removing pollutants from effluents.

The key tasks for the practical implementation of the method of cross-effects are: the availability (development) of tools that would provide research on water purification in real time; establishing a limiting environmental criterion that would take into account the resource consumption for water purification.

Dominant dynamic pollutant method

At the stage of analyzing the quality of wastewater purification of real enterprises and model solutions [23], a hypothesis arose that in order to remove some pollutants, it is necessary to first eliminate other pollutants, which critically reduce the removal effect of the former. Taking into account the research results, it was concluded that it is rational to propose the use of the dominant dynamic pollutant (DDS) method. That is, DDS is a multicomponent wastewater pollutant that, given the actual composition of the wastewater, must be removed first. The technical and economic modes of its elimination have been determined by the method of cross-effects. The presence of the next DDS is assessed and removed, and these steps are iteratively repeated to meet regulatory requirements for effluent quality.

Processing of research results

According to the Kolmogorov (Kolmogorov-Smirnov) criterion, the possibility of using parametric approaches of mathematical statistics was established [28]. Verification of compliance with the normality requirements of the law of distribution of random variables with an analysis of the presence of outliers in the information received at enterprises. The nonparametric approach and analysis of the Mann-Whitney test results are applied for all pairs of production approbation samples (Jonkhier U) statistics.

Results and discussion

Forming generalizing criterion of efficiency

Analysis of the logical model (see Figure 2) indicates (system-building blocks) that the key element for creating the TS is the development of a complex criterion for the efficiency evaluation of the use of electrotechnology wastewater purification means [25]. Herewith, technical efficiency (P) is calculated by the following formula:

$$P = \frac{(C_{in} - C_{out})}{C_{in}} \cdot 100\%, \quad (1)$$

where C_{in} is the value of the quality of wastewater under purification, and C_{out} is the concentration of contaminants after purification.

However, this approach to determining the efficiency takes into account the environmental component only, without considering the performance data which characterize the operation of the technological equipment. Taking into account the considerations presented in [4], it is apparent that the provision of a given level of wastewater purification can be implemented with various energy costs. Only comprehensive assessment of the operational efficiency of the technological equipment of wastewater purification will make it possible to find the boundaries of efficient energy resources use. On the basis of the conducted theoretical research and experimental tests [2-4] the basic criterion of energy efficiency has been obtained as follows:

$$EF_Y = \frac{\left[\left(\frac{L1_{out} - L1_{ref}}{L1_{out}} \cdot 100\%\right) + ... + \left(\frac{LN_{out} - LN_{ref}}{LN_{ref}} \cdot 100\%\right)\right] \cdot \sum_{i=1}^{N} Q_i}{\sum_{i=1}^{N} W_i} \text{ %/kWh}, \quad (2)$$

where L_{out} is the actual value of the corresponding wastewater purification quality assessment parameter; L_{ref} is a given (specified) value of the corresponding wastewater purification quality assessment parameter; Q is the equipment operating time in hours; W stands for electricity consumed by the electrotechnology wastewater purification equipment in kWh; N is the number of wastewater purification quality assessment parameters (they generally correspond to the number of plants involved into the wastewater purification process).

Technologically, the task of controlling the combined wastewater purification system is in maintaining the value of the energy efficiency criterion (2) close to zero: if $EF_Y>0$, the purification is unsatisfactory, if $EF_Y<0$, the use of energy resources is inefficient.

Justification intelligent control system

Automated information-measuring complexes of water purification systems, with the maximum layout for solving control problems can be divided into levels [2, 6]:

- the first level – means of obtaining information about the parameters of the technological control object (sensors);
- the second level – primary analysis devices (in some cases, the sensors and organs are inseparable – control actions from sensor regulators can be formed);
- the third level – means of centralized processing of information from sensors and regulators, as well as additional external information, for example, adaptive control algorithms and development of solutions for regulators in order to optimize the processes of obtaining specified quality criteria, including on economic requirements;
- the fourth level – a centralized control system for a whole complex of technological objects, provides control over the work of local systems of the third level, a statistical analysis of the quality indicators of individual units and the development on this basis of optimal (effective) solutions for specific third-level systems.

As a result of the research, the architecture of the control system with adaptive real-time control strategy adjustments with the possibility of making decisions under the effects of natural and man-caused disturbances, taking into account the energy efficiency criterion (2), has been developed. The generalized system includes a local control system and a decision-making subsystem with an input signal filtering unit (the decision-making subsystem contains a unit of adaptive real-time control strategy building based on Kohonen Self-organizing map).

The wastewater purification and wastewater purification equipment control system consists of a decision-making subsystem *1*, which includes an input signal filtering unit *2*, a unit for the neural network correction of fuzzy cognitive map (FCM) concepts *3*; a decision-making unit *4*, a unit of real-time adaptive forming of control strategies *5*, a control unit *6*; a local control system *7* consisting of a local automatic control device *8*, actuators *9* (electrolyzer, pumps, vacuum pumps, valves, heaters, compressors, etc.), a control object *10* (Figure 3). ICP DAS i-8417 PLC-class microcontroller (upper level), ATmega128-16AU microcontroller (lower level) [6] have been selected as control devices for the implementation of the instrumental information and measurement complex of the combined electrotechnology wastewater purification. C ++ programming software has been developed for these technical automation means with the use of the QT library in the Qt Creator programming environment.

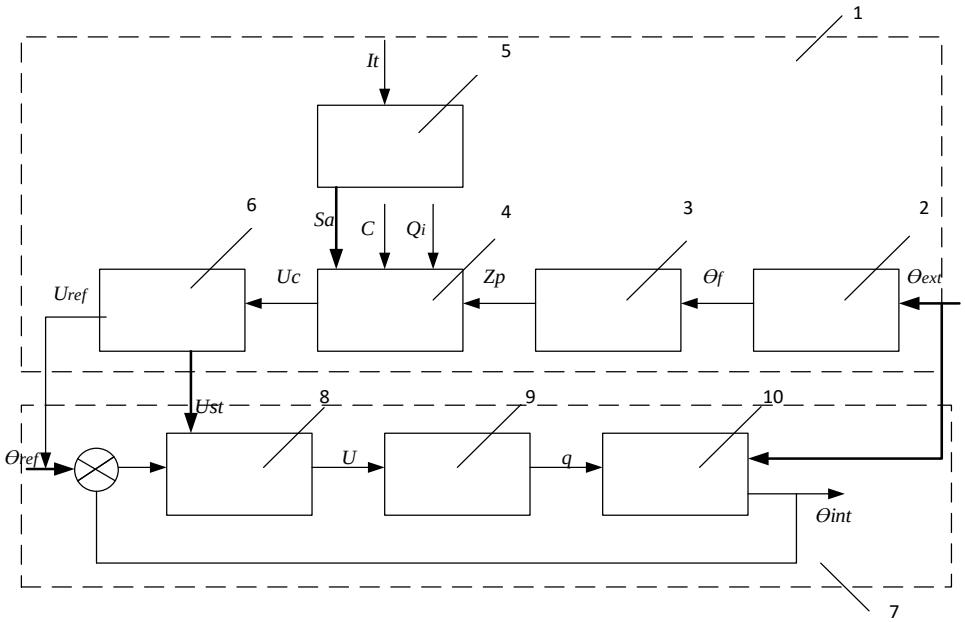

Figure 3. Architecture of the intelligent system of energy efficient control of the combined electrotechnology wastewater purification:

θ_{ext} – signal from the sensing elements;
θ_f – stands for the cleared information signals;
Z_p – stands for perturbations;
Q_i – stands for possible control actions and quality indicators;
C – cost data of the components of the electrotechnology process;
U_c – choice of the control strategy;
U – current control strategy;
I_t – information entered by process control operators;
S_a – updated set of strategies;
U_{ref} – change in control;
U_{st} – stands for new images of the control strategy;
θ_{ref} – given value for control;
θ_{int} – generated control value;
q – stands for the influence on the water purification plants.

Analysis of test results

The production testing of the control system was conducted at the enterprises of meat processing and minor metallurgy. Water passports and TS were previously developed for such enterprises [20, 26].

On the bases of the use of the working standard of the combined electrotechnology wastewater purification equipment for the meat processing enterprise, daily doses of contaminants (DDC) – fats (daily consumption – 1500 m^3/day (± 300 m^3/day [3]) have been defined. However, fats are organic contaminants and their complete removal does not provide for the purification of the wastewater from ammonia nitrogen, phosphorus and chlorides. Therefore, it is necessary to select DDC for inorganic contaminants, proceeding from the previous research [1, 26], the one adopted here is the "chlorides concentration" being the most difficult contaminant to be removed.

When using combined wastewater purification systems for meat processing enterprises (DDS – fats), it was experimentally calculated [24] that as a result of the removal of such DDS, the concentration of other pollutants decreases by at least 50-95% (depending on the initial concentrations of pollutants).

The occurrence of emergency situations in wastewater purification systems at the meat processing enterprise is due to the following:

- Slaughter above the norm (leads to significant exceedances in the concentration of fats, phosphorus, ammonium nitrogen and increased turbidity of the wastewater);
- Additional washing of the technological equipment (occurs at regular intervals and leads to significant exceedances in concentrations of synthetic surface-active substances (ssas) and turbidity of the wastewater);
- Emptying of the skin salting tanks (occurs at regular intervals and results in significant exceedances in chloride concentrations).

The implementation of the developed TS for the operation of the electrotechnology wastewater purification system, which includes electroflotocoagulation, electrolysis destruction, sorption filtration, sedimentation and hydrocycloning, has made it possible to fully meet the requirements for maximum permissible concentrations of contaminants in the wastewater of the enterprise (Figure 4).

Adjusting the equipment to meet the developed energy efficiency criterion (2) has made it possible to meet the requirements for wastewater purification quality while minimizing the resource costs – the energy efficiency criterion (2) within a period of a month (October 2016) had a deviation from zero ± 9,6 % (including operation under uncertainty conditions caused by the effect of emergency situations) (Figure 5).

The daily wastewater amounts of minor metallurgy enterprises which require purification equal 18 m^3/day (± 2 m^3/day). Following on from the use of the the working standard of the combined electrotechnology wastewater purification equipment, DDC for the wastewater of the minor metallurgy enterprise has been estimated – SPAR (Synthetic surfactants). Experimental simulation has determined that the removal of SPAR will securely remove such contaminants as ammonia nitrogen and petroleum derivatives [24].

Emergency situations can be caused by the penetration of accidental contaminants into wastewater [27]. That is why the electrocoagulator with the function of pH-correction of alkaline solutions with subsequent neutralization of the wastewater and a sorption filter, a deaerator with electrolysis destruction and hydrodynamic intensifiers have been included into the combined electrotechnology wastewater purification system.

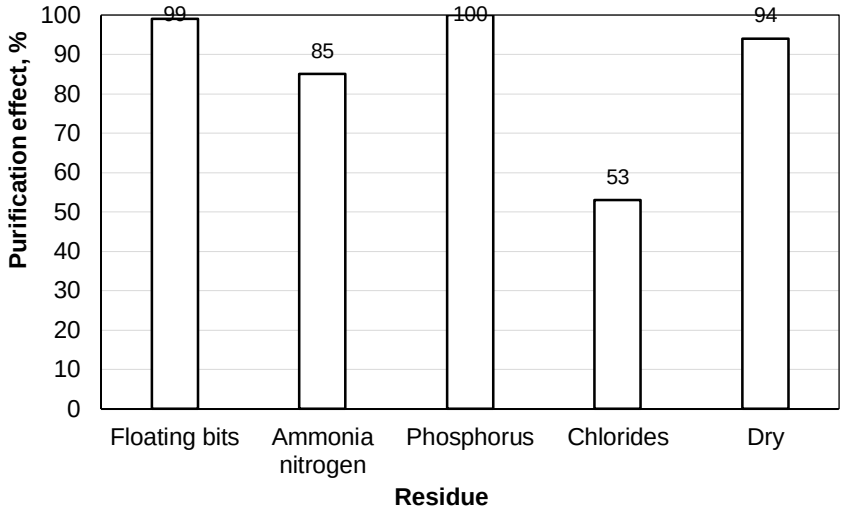

Figure 4. Efficiency of the combined electrotechnology wastewater purification (using the example of a meat processing enterprise)

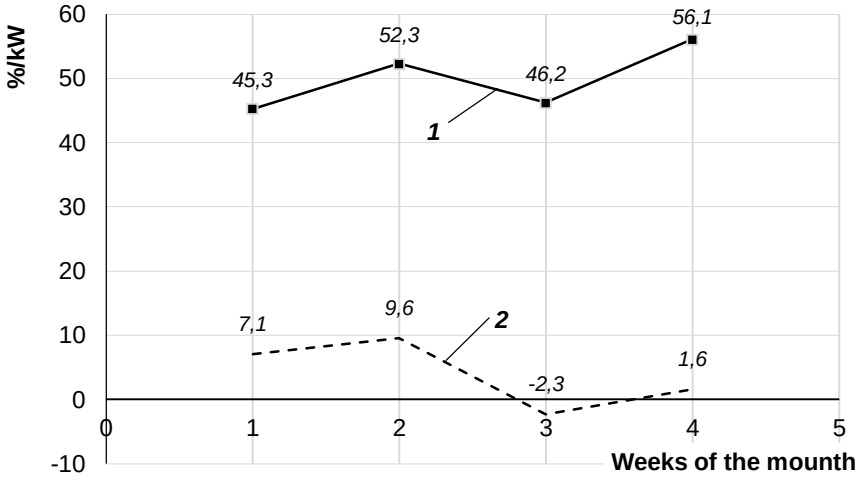

Figure 5. Comparison of the energy efficiency of the electrotechnology industrial wastewater purification (using the example of a meat processing enterprise):
1 – before implementing the control system and the technological complex (September 2016);
2 – after implementing the control system and the technological complex (October 2016)

According to the Kolmogorov (Kolmogorov-Smirnov) criterion [28], it was found that it is impossible to apply parametric approaches to the data samples obtained at the meat processing plant. The results of the work of the modeling complex of industrial water purification by the parameter of water quality "Concentration of nitrates" were selected and it was found that the significance of the results was less than 5 % (actually 0,5 %). The

statistical assessment of the data of the water passports of the studied enterprises showed that not all the obtained samples of the values of pollutants meet the requirements of the normality of the law of distribution of random variables (about 20 % do not correspond). At the same time, the absence of emissions in the information received at the enterprises was established.

Applying nonparametric approaches and analyzing the results of the Mann-Whitney test for all pairs of industrial samples of approbation (Jonkhier U) statistics and the probability of accepting the hypothesis H0(p) and the distribution of samples of energy efficiency of various reactions), we came to the conclusion that the hypothesis H0 is accepted (the smallest values U = 46,5, p = 0,790953), all datasets are homogeneous [28]. The results of the work of the intelligent information-functional model are acceptable and the model can be used at industrial facilities, for example, as a decision support system.

Adjusting the equipment to meet the energy efficiency criterion (2) has made it possible to meet the requirements on ensuring the quality of wastewater purification at the lowest possible energy costs (Figure 6).

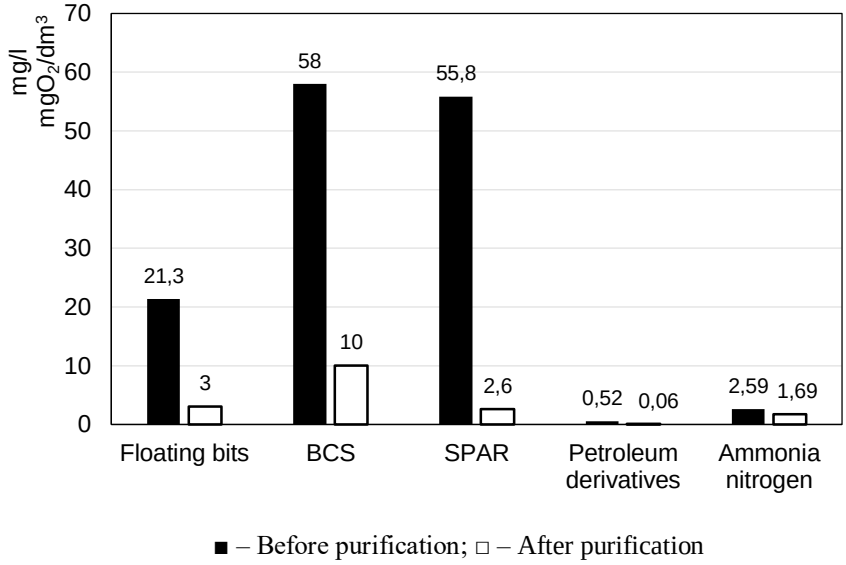

Figure 6. Combined system of electrotechnology wastewater purification (using the example of a minor metallurgy enterprise)

Production observations of the wastewater purification processes with determination of the level of energy consumption during the solar month has provided an opportunity to obtain the deviation of $EF_Y = \pm 3{,}4$ % (Figure 7).

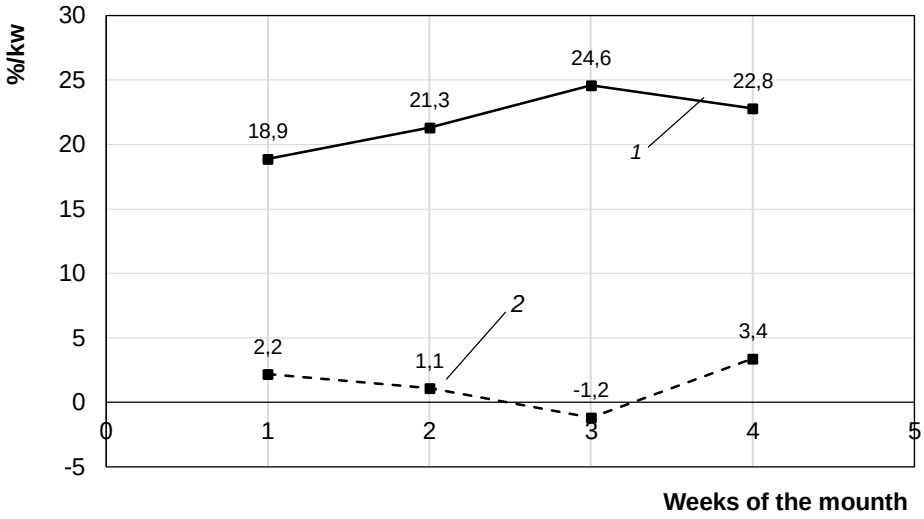

Figure 7. Comparison of energy efficiency of the electrotechnology industrial wastewater purification (using the example of a minor metallurgy enterprise):
1 – before implementing the control system and the technological complex (February 2017);
2 – after implementing the control system and the technological complex (March 2017)

After analyzing the results of the industrial implementation of the energy efficient industrial electrotechnology wastewater purification systems at meat processing and minor metallurgy enterprises, it can be stated that the improved method [26] has provided an opportunity to fulfill the ecological requirements as to the quality of the wastewater discharge while meeting the energy efficiency (2). Such industrial enterprises have also been provided with the opportunity to reuse the purified wastewater in technological processes (e.g. equipment washing and irrigation of the territory), thereby increasing the resource efficiency.

It has been confirmed that system-building elements of the advanced approaches of the TS synthesis of the combined electrotechnology wastewater purification are working standard of the combined electrotechnology wastewater purification and the DDC method (see Figure 2); at the same time, their object-oriented use is to be based on creation, as a result of systematic assessment of the objects of the wastewater discharge, the water passport. Having regard to the above, it can be claimed that not fully complying with the energy efficiency requirements (see Figs. 5 and 7), caused by an insufficiently long-lasting study of the enterprises, which were under testing, the broadening of the informative base of the major research is crucial for the improvement of the energy efficiency.

Conclusions

1. The integrated use of the improved scientific and theoretical foundations of electrotechnology management for water purification makes it possible to improve the methods of removing pollutants from aqueous solutions by comprehensively accounting for the mutual influence of methods and techniques for their elimination.

2. The use of the advanced methods of synthesis of the TS for wastewater purification systems at continuous production has made it possible to introduce resource-saving schemes of wastewater discharge (re-use of water in technological processes).
3. Practically implemented approaches aiming at improving the creation and operation of the combined electrotechnology wastewater purification systems of continuous production have improved the energy efficiency of processing multi-component wastewater discharges: for meat processing enterprises the deviation of the energy efficiency criterion from zero makes ± 9,6 %, ± 3,4 % for minor metallurgy enterprises.
4. The analysis of the results obtained from the operation of the created wastewater purification systems at the continuous production has shown that the proposed approaches to the TS synthesis give an opportunity to reduce the negative effects of the man-caused and natural emergency situations, by means of using the equipment for setting up the combined electrotechnologies of wastewater purification and taking into account the DDC method in information-functional simulation.

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Assessment of the development level of corporate social responsibility of a company

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Abstract

Introduction. It has been analyzed the existing methodologies for the assessment of corporate social responsibility (CSR) efficiency.

Materials and methods. For the current studies of the level of the enterprise's CSR development were used qualitative and quantitative methods of study for Ukrainian food processing enterprises. The CSR must be assessed by directions. Each of these levels has its own system of quantitative and qualitative indices and different methods, which may be used.

Results and discussion. The paper proposes the improved methodology for the determination of the CSR efficiency integral index, which is calculated by using the system of qualitative and quantitative parameters of the CSR assessment, which unlike the existing ones, take into account the indices of the internal and external CSR form.

The quantitative parameters of the internal CSR include such groups as the satisfaction of owners' interests through the company's profitability (the coefficient of changing the assets profitability), the satisfaction of personnel's interests (the coefficient of changing the employees' average monthly salary), the social investments on internal programmes (the coefficient of changing the expenses on internal social programmes), personnel development (the coefficient of changing a part of employees who completed re-training courses or advanced training), etc. The quantitative parameters of the external CSR include such groups as the social investments in outdoor environment (the coefficient of changing the expenses on external social programmes), the social investments on ecological programmes (the coefficient of changing the expenses on ecological programmes). The value of the coefficient of qualitative parameters is calculated according to the enterprise's CSR development level at the moment of the research.

Conclusion. The value of the integral index allows determining the level of the enterprise's CSR development and work out the system of measures for the development of the company's social activities.

Introduction

Many scientific works are dedicated to the issue of corporate social responsibility (CSR) of companies as well as CSR efficiency assessment. However, these researches mostly deal with two principal approaches to the enterprises' CSR assessment: by quantitative and qualitative indices of social activities and influencing upon financial and production indices. Thus it is necessary to choose those methods and methodologies which will allow conducting the qualitative and quantitative assessment for the state of internal and external CSR, and the integral assessment will serve for the comparison and determination of the company CSR efficiency. G. Bowen considers the corporate social responsibility for an entrepreneur to be "the implementation of such a policy, making such decisions or observance such a behavior, which would be desirable for the purposes and values of a society".

There is the need to develop the complex methods for the company CSR assessment and the obtained results can be used both in the corporate social activity management and when forming the companies' ratings. And this causes the particular relevance and practical value for studying the current issues.

Materials and methods

Materials

The object of the study is the process of assessing the level of development of the corporate social responsibility of the Ukrainian food industry enterprises.

The subject of the study is determining a system of indicators that will allow estimating the state of corporate social responsibility, taking into account the sectoral peculiarities of activity of the food industry enterprises.

The calculations on Integral index of CSR efficiency were tested on five companies of food industry for 2015–2017 years:

1. JSC «Zhytomyr Butter Processing and Packing Factory», sity Zytomyr, Ukraine;
2. JSC «Zhytomyr Integrated Bakery», sity Zytomyr, Ukraine;
3. LLC «Organic Milk», sityBaranivka, Zytomyr region, Ukraine;
4. LLC «Zhytomyr Meat Processing and Packing Factory», sity Zytomyr, Ukraine;
5. JSC «Beer-Alcohol-Free Plant «Radomyshl'», sity Radomyshl', Zytomyr region, Ukraine.

Methods

The research is based on the use of general scientific and special methods, i.e. strategic analysis is used to determine the impact of corporate social responsibility initiatives on the strategic position of the enterprise [5]; factor analysis is used to determine the direction and strength of the impact of individual factors influencing the development of corporate social responsibility [10, 26]; analysis and synthesis is implemented to develop a system of indicators and structuring the components of indicators to assess the level of development of corporate social responsibility [8, 28]; rating assessments is applied to assess the business reputation of companies [20,21]; peer review is used to determine the compliance with mandatory legal requirements and business ethics, the level of charitable and / or sponsorship activities, the level of responsibility of the company to internal and external stakeholders.

Literature analysis

G. Bowen considers the corporate social responsibility for an entrepreneur (Bowen, 1953) [1]. The role of CSR has been constantly increasing more and more in the development of society for several past years (Bartok, 2018; Burianová & Paulík, 2014) [2,3]. Scientists pay a lot of attention to the issues of social responsibility of business, its role in the solution of social, ecological problems of society (Khoma, Moroz, Horyslavets, 2018) [4], the study of connection between the CSR efficiency and financial indices, the maximization of value for stakeholders etc. (Rajnoha, Lesnikova, 2016) [5]. All these issues are more or less determined by the CSR development level. However, the character of interrelation between the interests of business and society, stakeholders has not been examined enough yet (Freeman, Harrison, Wicks, 2007) [6], Agle et al. (2008) [7], Schwartz & Carroll (2008) [8].

However many scientists consider that the theory of interested parties is connected to the impact of the initiatives on the management of stakeholders (Harrison, Bosse, Phillips, 2010) [9].

More questions and discussions appear when forming specific indices, which are used for measuring the CSR development level, the level of influence of social initiatives on social efficiency, corporate financial results. The issue of individual and corporate social responsibility, the impact of any initiative on strategic decisions were the subjects of scientific research (Bénabou, Tirole, 2010) [10].

The existing connection between the CSR development level and financial indices are introduced in modern investigations by many scientists (Bettis, Helfat, Shaver, Zhao, Murrell, 2016; Shahzad, Sharfman, 2017) [11,12].

In 1974 American scientists published the book "Unsteady Subsoil: Social Policy of Corporations in a Dynamic Society" while researching the issue of companies' CSR assessment (Robbins, Coulter, 1974) [13], where they singled out four approaches (methods) to the company CSR assessment. The first method involved the use of social indicators, the determination of living standard index through the calculation of quantitative indices and the assessment of corporations' social activity impact on this index (they are the indices of labour protection state, health protection state, and others), in particular. The second method was in developing the system, which included the assessment of expenses for the social programmes, their implementation, and their efficiency assessment as well. In F. Kotler's point of view, the CSR benefits are impossible to measure and the most companies do not disclose the expenses at such activities, and that is why it is impossible to measure the recoupment of such investments. The third method included carrying out the assessment through making up so-called social report, where the benefits for employees, customers, suppliers, community, and other stakeholders, the social expenses of a firm for providing these benefits were presented in the balance form. The fourth one is the method of ranking companies according to their social activities. First two approaches allow examining the CSR assessment from the point of view of external and internal CSR. Hence, in accordance with the significant expenses on social goals, we face the CSR efficiency assessment issue. The majority of advanced companies and consultants of the USA follow "a social audit", which focuses on how the company social behavior reflects on business indices. The methodology developed by the consulting company SmithOBrien requires the integrated activity assessment by the following principal systems of economic and social indices as the quality management system, energy-saving, and environmental protection, relations with personnel, human rights, and relations with local community (Nikitina, Borzakov, 2015) [14]. This methodology is the corporate stability audit integrated system implemented in all the international systems of social

responsibility ratings. As for the third approach, in our opinion, the availability of the social report itself can be examined as one of the CSR integrated assessment criteria. It is well known that the most used international standard for preparing the social reporting is the Global Reporting Initiative (GRI, 2015) [15]. This standard includes a sufficient amount of indices, but it does not deal with obtaining any common value of social responsibility level. The essential drawback of this standard is the application of various indices, expensive, natural, absolute, and relative. However, the advantage of the standard is increasing the prestige of company in the eyes of society that results in growing demand, consumers' credit, and finally increasing the products of company activities. It is important to publish and place the social reporting of companies on their web sites, present it on conferences, public events, even to issue brochures etc. Reporting is the main source of information about the company CSR.

These three approaches provide an opportunity to assess each component of social responsibility separately, but make it impossible to assess the general level, and compare companies quantitatively. For this purpose, the above-mentioned rating approach is used. In addition, competitions and ratings must be maximum transparent and open as well as their organization performance must be professional, responsible, and sustainable (prestige, reputation, independence etc.).

Nowadays, reputation ratings are used in the world (the fourth approach). The rating method involves ranking the group of companies with similar type of activities by determined criteria. Professionals of any field of research, groups of consultants, public organizations, independent experts etc. can function as experts. The rating of companies' business reputation for all the countries, but the USA, has been composed since 1997 by Hoy Groupp agency. The experts assess over 300 companies. The assessment is carried out on innovations, personnel, using corporate assets, social responsibility, management quality, financial sustainability, long-term investments, the quality of products and services. Among the first ones there are companies, which know how to build up their relationships with stakeholders, i.e. the first places are not always given to the companies with the highest amount of sales, income etc. (Beliaeva, Eskindarova, 2016) [16].

Most scientists involved in studying the issues of assessment of corporate social responsibility development level consider that the CSR must be assessed by directions and different methods may be used simultaneously. They single out personnel and its development, environmental protection activities, health protection and working conditions, the development of communities, resource-saving, and business practice. And each of these directions has its own system of quantitative and qualitative indices.

Vorona (2010) has the same opinion and adds that it is necessary to single out the following four directions: personnel, business, a society, and an image, and determine corresponding indices for the CSR assessment [17]. Levyts'ka (2012) also proposes to assess the CSR efficiency by directions. However, the author's rather unusual classification of directions presents the indices: expensive (assess the level of expenses on social actions), resulting (assess the effect from the implementation of social actions), structural (assess the change of the structure of a definite resource), effective (assess the ratio of result and expenses) [18].

In the articles of Buian (2012) special attention is being paid to the international methods of assessment and some specific methods for the CSR assessment are singled out, i.e. World Stock Dow Jones Sustainability Index, Social Index – SI of Danish Ministry for Social Policy, Corporate Philanthropy Index, Triple Bottom Line Method, Balanced Scorecard Method, FTSE4Good Index, Domini Social Investment Index (DSI 400) and others. The researcher adds that in spite of their spreading in the countries of North America

and the European Union, they are difficult to be used for the assessment of the CSR level concerning domestic enterprises. There are differences in directions and parameters, and each approach and method allows to analyze a definite component only or the group of CSR components [19].

In addition, at present there are variable methods for the assessment of CSR of enterprises. Kusyk (2012) states in the publications that some researchers follow the methodology developed by the Association of Russian managers with the support of UNO Development Programme in order to determine the influence of the company social responsible activities [20]. It is suggested to measure the quantitative index of business social investments:

- The index of specific social investments is the value of companies' social investments per employee;
- The ratio (share) of company social investments to the total amount of their sales (per cent);
- The ratio (share) of company social investments to the total amount of their incomes (before taxation) (per cent).

The amount of quantitative measurement of social investment index is not standardized and may have any positive values. However, the high level of index proves the high level of company social activity.

Unlike the quantitative indices of social investments, which create the picture of the phenomenon scope, the qualitative index of social investments includes the assessment of the level of complexity and fullness of such a phenomenon as corporate social responsibility. In this case, they use three groups of criteria for the quantitative assessment of social investments and these groups are based on 12 indices that allow calculating the following types of the qualitative index of social investments:

1. The qualitative index of social investments for i-company showing the level of complexity of the company social activities (per cent);
2. The qualitative index of social investments for j-feature showing the degree of the qualitative feature availability in the selection of companies – respondents (per cent);
3. The general qualitative index of social investments showing the level of complexity of the social activities for the company, which is researched (per cent).

All these three kinds of the qualitative indices of social investments are standardized and may accept values from 0 % to 100 %. The value of the index is higher the more complete and integrated the company social policy is.

According to the point of view of above-mentioned article this methodology can be used for building the rating among the enterprises engaged in social responsible activities, but the model described by Shmygol (2010) is considered to be more reasonable; this model for the assessment of efficiency of social investments and corporate social responsibility was developed by the scientists from "The Institute of City Economy" and shows the calculation of the integrated index [21].

The integrated index is calculated as the ratio of the amount of paid out taxes, investments in fixed capital, and company social expenditures to the current expenses of production purposes. Besides, the indicator of perspective development is calculated as the ratio of the amount of investments in fixed capital and social expenditures to the company net profit. The indicator of social expenditures is calculated as the ratio of amount of social expenditures to the net profit for a reporting period (the index showing 1% is considered to be ordinary).

One should agree with Khlevyts'ka (2014) saying that it is necessary to apply a comprehensive, integral assessment of totality of separate indices, which reflects the key

aspects of the company activities in the CSR area to the maximum. The methodology offered by her includes the calculation of intermediate integral indices (about economic efficiency of activities in the CSR area, about social efficiency of activities in the CSR area, about ecological efficiency of activities in the CSR area), and generalizing integral index of CSR activity efficiency [22].

The author of the article considers that the most reasonable is the determination of the significance of the indices by the expert's way that allows underestimating the objectivity of the performed calculations. In addition, the researcher does not provide the mentioned limited indices by components: economic, social, and ecological. If interpreting the obtained results of the integral assessment of efficiency of activities in the CSR area takes place and the enterprise observes all the standard values, then the value of the integral index is equal to 1. The methodology proposed by Khlevyts'ka [22] composes the general integral index; on the other hand, this methodology is not easy enough for implementation and requires the involvement of experts.

The view of empirical investigations of corporate social responsibility dedicated to the study of relationship between corporation and society with the application of social ratings of such companies as Kinder, Lydenberg, Domini for the period before 2011 were presented by Mattingly (2017) [23]. The view generalizes 100 empirical investigations, describes their peculiarities and discrepancies, but this particular study did not allow to solve the issue methodologically.

Methodological issues relating to reporting biases and sample selection biases in CSR research are taken up by Rost and Ehrmann (2017) [24] and Shahzad and Sharfman (2017) [12] respectively. The issue concludes with a research note on the weighting of CSR dimensions by Capelle-Blancard and Petit (2017) [25].

The study of A. Crane, I. Henriques, B.W. Husted and D. Matten was dedicated to the improvement of the methodology concerning the CSR assessment on the base of quantitative methods (Crane, Henriques, Husted, Matten 2017) [26].

In our opinion, the paper published in 2018 is considered to be rather interesting investigation (Halme, Rintamäki, Knudsen, Lankoski, Kuisma, 2018) [27]. It presents the qualitative comparative analysis based on 19 big companies. It determines various ways connected to the improvement of ecological and social indices in the CSR area. It reveals two ways for improving the ecological indices: exogenous and endogenous. The paper also shows the ways of improving the social indices, which include the integration of social responsibility in main business.

Results and discussion

Performing the CSR assessment first of all it is necessary to determine the tasks of the assessment and choose the methods and use the methodology according to the purposes (strategic, current, rapid analysis), activity directions (internal CSR and external CSR), and users' needs (owners, investors, managers, stakeholders, Government). Moreover, the indices must be both quantitative and qualitative. The external rating assessment of the companies' business reputation is significant. At present, there are a number of ratings in the entire world with their criteria of assessments. However, there should be mentioned that the assessment is conducted mainly on investments, personnel, the use of corporate assets, social responsibility, the quality of management, financial sustainability, long-term investments, the quality of goods and services, etc. The information about the company activities as mentioned above is presented mostly by indices (calculation indices), which allow to

transform a public conception concerning the company responsibility to ethical, social requirements into a specific index. They are social indices, stock, and non-stock. The concept of sustainable development singles out three directions applied for the formation of ratings and corresponds to the CSR concept:

1. Positive characteristics of the company production and economic activities;
2. Ecological characteristics and the decrease of negative impact on environment;
3. The company social development and its social policy implementation.

Moreover, there is another important point that concerns the realization and observance of the CSR standards, which influences in particular the formation of indicators in the CSR area.

Development of research methodology

According to the results of the carried out investigation, we suggest determining the integral index of corporate social activity efficiency, which will show the impact of both qualitative and quantitative indices.

The integral index will be determined by the following formula:

$$\text{ІП}_{\text{КСВ}} = \text{С}_{\text{CSR}}^{\text{qualit}} = \text{С}_{\text{CSR}}^{\text{quant}} \quad (1)$$

where ІІ_{CSR} : the integral index of the company CSR efficiency;

$\text{С}_{\text{CSR}}^{\text{qualit}}$: the coefficient of the qualitative parameters of the CSR efficiency;

$\text{С}_{\text{CSR}}^{\text{quant}}$: the coefficient of the quantitative parameters of the CSR efficiency.

$$\text{С}_{\text{CSR}}^{\text{quant}} = \frac{\text{С}_{\text{CSR}}^{\text{intern.}} + \text{С}_{\text{CSR}}^{\text{extern.}}}{2} \quad (2)$$

where $\text{С}_{\text{CSR}}^{\text{intern}}$: the coefficient of the internal social policy efficiency,

$\text{С}_{\text{CSR}}^{\text{extern}}$ – the coefficient of the external social policy efficiency,

$$\text{С}_{\text{CSR}}^{\text{intern}} = \text{С}_{\text{profit.asset.}} \text{ x } \text{a}_{\text{profit.asset.}} + \text{С}_{\text{S}} \text{ x } \text{a}_{\text{s}} + \text{С}_{\text{EISP}} \text{x } \text{a}_{\text{EISP}} + \text{С}_{\text{ETR}} \text{ x } \text{a}_{\text{ETR}} \quad (3)$$

where $\text{С}_{\text{profit.asset.}}$: the coefficient of changing the company assets profitability;

С_{S}: the coefficient of changing the company employees' average monthly salary;

С_{EISP}: the coefficient of changing the expenses on internal social programmes;

С_{ETR}: the coefficient of changing a part of employees' quantity who completed re-training courses or advanced training,

$\text{a}_{\text{profit.asset.}}$, a_{s}, a_{EISP}, a_{ETR},: the significant coefficients showing the importance of the parameter when the internal CSR efficiency assessment takes place.

$$\text{С}_{\text{CSR}}^{\text{extern}} = \text{С}_{\text{EESP}} \text{ x } \text{a}_{\text{EESP}} + \text{С}_{\text{EEP}} \text{ x } \text{a}_{\text{EEP}}, \quad (4)$$

where С_{EESP}: the coefficient of changing the expenses on external social programmes;

С_{EEP}: the coefficient of changing the expenses on ecological programmes; a_{EESP}, a_{EEP}: the significant coefficients showing the importance of each parameter when the CSR efficiency assessment takes place.

Dumova L.V. mentions that the qualitative features of the CSR efficiency are mainly based on the regulations of international organization «Global Initiative on Reporting» and contain such criteria as the availability of the collective contract; the availability of general

papers regulating the company CSR activities; the availability of annual public reporting on the company social activities and its publication on the site; the availability of the appropriate department (in the organizational structure), which is responsible for the company social activities (Dumova, 2014) [24].

Examining the qualitative features according to the levels of the CSR development, we may single out the most important ones:

- the first level (basic). The observance of the requirements for this basic level allows the enterprise to run its activities within the limits of the obligatory legislative requirements and ethical rules of business;
- the second level (the level of charitable / or sponsoring activities);
- the third level (the level of company responsibility before internal and external stakeholders). The public reporting on social activities and placing the results on the company site and in mass media;
- the fourth level (the level of strategic direction of CSR and social investments). Observance of three mentioned above CSR levels allows the companies to reach the qualitatively new level of the CSR development, i.e. implementation and observance of the CSR European standards. The development of the strategy of social responsible measures and its integration in the company development strategy;
- the fifth level (the level of the CSR synergistic effect). Not all companies can reach the fifth level of the development. That is why we are not going to use it for the assessment. According to the presence or absence of the features, which are presented for each level, the value of K_{CSR}^{qualit} coefficient is determined.

Determining of the influence of the CSR on the business reputation of the company (Lahuta, 2017) [29] was conducted according to the results of questioning of 18 food industry enterprises. The value of the coefficient of qualitative parameters was determined basing on the level of development of the CSR. The figures are presented in the Table 1.

Table 1

Measurement of the coefficient of qualitative parameters according to the CSR level at an enterprise*

Level of development	Requirements	Value of the coefficient of qualitative parameters C_{CSR}^{qualit}
The first level	Observance of the features of the first level	0,25
The second level	Observance of the features of the first level and additional ones of the second level	0,5
The third level	Observance of the features of the first and second levels and additional ones of the third level	0,75
The fourth level	Observance of the features of all previous levels and additional ones of the fourth level	1,0

**Note: compiled by the authors*

The quantitative indices of the CSR efficiency determined according to the development directions are divided mainly into two big groups:

1. Internal CSR (personnel and owners, quality and innovation, labour protection and safety);
2. External CSR (local communities, ecology)

The quantitative indices are coefficients determined as the ratio of the corresponding indices in the analyzing and basic periods. For the parameters, which are measured by valuable indices, we take into account the inflation index through the use of the discounting coefficient (Id). We developed the system of indices for determining the coefficients of measurement for the quantitative parameters of the company CSR efficiency, which includes economic, social, and ecological constituents (Table 2).

The coefficients of significance determined due to the results of the conducted questioning are equal by two criteria (assets profitability and average monthly salary – 0,25), the index of expenses on internal social programmes in experts' opinion is considered to be the most important, that is why it possesses 0,3. The index characterizing a part of employees who completed re-training courses or advanced training shows the lowest coefficient of significance – 0,2. The indices concerning innovative activities, the quality of goods, and anti-corruption activities possess qualitative characteristics, thus these indices were already included into the group of qualitative parameters.

To assess the external CSR we use such quantitative indices as the expenses on external social programmes and expenses on ecological programmes.

Experts consider the used indices to be equal in value, thus weighting coefficients of their significance are 0,5. The value of these coefficients is determined by the expert way and depends on the company peculiarity, thus the assessment model itself obtains the features of universality.

Taking into account the results of the previous investigations (Lahuta, 2018) [30], we determine the following levels of the CSR development:
when:

$0 < II_{CSR} \le 0{,}25$ – the enterprise possesses the low level of the CSR efficiency, or when $II_{CSR} = 0$, – such activities are absent (initial I level);

$0{,}25 < II_{CSR} \le 0{,}5$ – the enterprise realizes social policy, but on an average level (II level);

$0{,}5 < II_{CSR} \le 0{,}75$ – the social policy of the company has the average level of social activities (III level);

$0{,}75 < II_{CSR} \le 1{,}0$ – the enterprise possesses the high level of social activities (IV level);

$II_{CSR} > 1{,}0$ – the enterprise has the high level of social activities and such activities has a synergetic effect, aimed at the increasing of the company business reputation level in outdoor environment.

Table 2

Measurement coefficients of quantitative parameters of the company CSR efficiency*

Name of group of quantitative parameters	Name of coefficient	Formula for calculation	Coefficient significance(k)
Internal CSR			
Satisfaction of owners' interests through the company profitability	Coefficient of changing the assets profitability ($C_{profit.asset.}$)	$\frac{C^{act}_{profit.assets}}{C^{baz}_{profit.asset}}$	0,25
Satisfaction of personnel's interests	Coefficient of changing the employees' average monthly salary (C_S)	$\frac{C_S^{act}}{C_S^{baz} \times I_d}$	0,25
Social investments on internal programmes (labour protection, working conditions etc.)	Coefficient of changing the expenses on internal social programmes (C_{EISP})	$\frac{EISP_{act}}{EISP_{baz} \times I_d}$	0,3
Personnel development	Coefficient of changing a part of employees who completed re-training courses or advanced training (C_{ETR})	$\frac{C^{act}_{ETR}}{C^{baz}_{ETR}}$	0,2
External CSR			
Social investments in outdoor environment	Coefficient of changing the expenses on external social programmes (C_{EESP})	$\frac{EESP_{act}}{EESP_{baz} \times I_d}$	0,5
Social investments on ecological programmes	Coefficient of changing the expenses on ecological programmes (C_{EEP})	$\frac{EEP_{act}}{EEP_{baz} \times I_d}$	0,5

**Note: compiled by the authors*

Analysis of caculations

The calculations on this model were tested on five companies of food industry in Ukraine. Indicators for determining the efficiency coefficients and the quantitative parameters for calculating the integral indicator of CSR efficiency are presented in Tables 3. The results of calculation for the integral index of corporate social responsibility efficiency are shown in Table 4 and presented in Figure 1.

Table 3

Indices for determination of the coefficients of qualitative and quantitative parameters to calculate the integral index of CSR efficiency of enterprises for 2015-2017

Indices	JSC «Zhytomyr Butter Processing and Packing Factory»			JSC «Zhytomyr Integrated Bakery»			LLC «Organic Milk»			LLC «Zhytomyr Meat Processing and Packing Factory»			JSC «Beer-Alcohol-Free Plant «Radomyshl'»		
	2015	2016	2017	2015	2016	2017	2015	2016	2017	2015	2016	2017	2015	2016	2017
Enterprise's assets profitability*,%	12,1	14,7	15,3	-21,2	-30,8	-21,0	14,8	16,8	17,3	1,6	0,8	5,3	-2,1	-9,5	1,3
Employee's average monthly salary, thousand monetary units	6200	6580	8900	2320	2537	3400	4050	4652	4900	4500	4800	5300	5490	6800	7070
Expenses on internal social programmes, thousand monetary units	95320	112780	56300	1200	2766	1450	850	1250	970	1100	1230	1200	256	989	950
Part of employees who completed re-training courses or advanced training, % to general amount of employees	15,1	14,1	18,4	8,2	2,3	7,9	5,1	5,4	8,3	2,0	4,1	10,1	12,1	11,2	8,7
Expenses on external social programmes, thousand monetary units	860,5	1112,1	1500,6	88,1	100, 2	90,7	230,2	210,4	270,4	330,8	310,7	390,7	450,1	560,4	778,4
Expenses on ecological programmes, thous. hrv.	678,0	560,9	847,5	123,1	100,9	88,9	67,9	69,7	88,9	98,7	110,5	125,4	256,8	240,5	334,8
Average inflation index per year**, %	143,3	112,4	113,7	143,3	112,4	113,7	143,3	112,4	113,7	143,3	112,4	113,7	143,3	112,4	113,7

*If the value of profitability index gets " – ", then we calculate the value of the coefficients as zero.
**Index data was obtained according to the information [31].

Table 4

Integral index of corporate social responsibility efficiency of Ukrainian companies for 2015-2017* (according to the results of selection)

Years	Value of integral index for companies				
	JSC «Zhytomyr Butter Processing and Packing Factory»	JSC «Zhytomyr Integrated Bakery»	LLC «Organic Milk»	LLC «Zhytomyr Meat Processing and Packing Factory»	JSC «Beer-Alcohol-Free Plant «Radomyshl'»
2015	0,83	0,20	0,68	0,23	0,21
2016	0,74	0,23	0,79	0,26	0,31
2017	0,80	0,24	0,77	0,46	0,28

**Note: compiled by the authors according to the results of the researches*

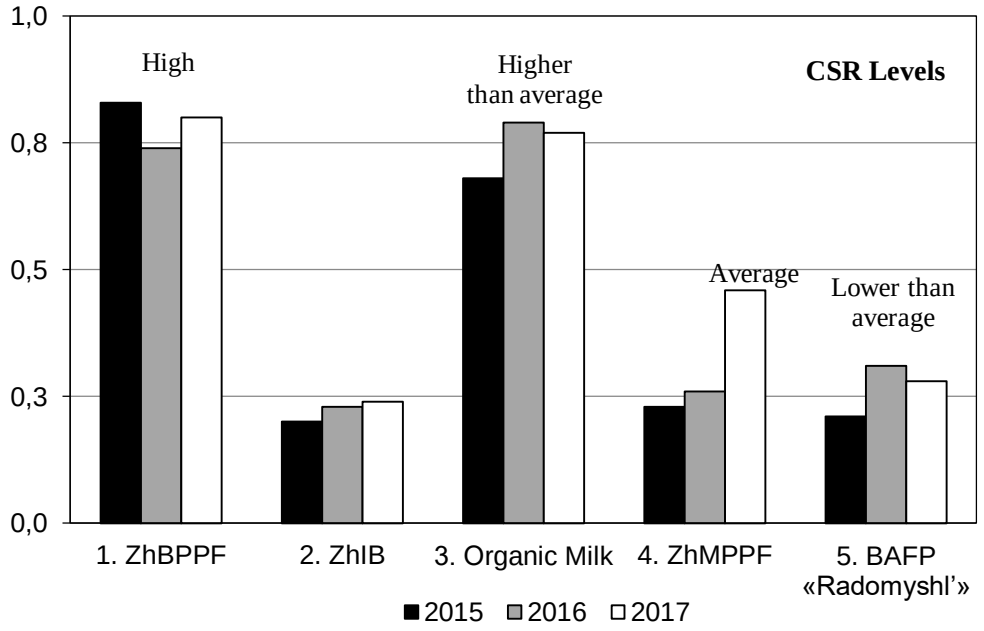

Figure 1. Value of integral index of companies' CSR efficiency for 2015-2017*

1. JSC «Zhytomyr Butter Processing and Packing Factory»
2. JSC «Zhytomyr Integrated Bakery»
3. LLC «Organic Milk»
4. LLC «Zhytomyr Meat Processing and Packing Factory»
5. JSC «Beer-Alcohol-Free Plant «Radomyshl'»

**Note: compiled by the authors according to the results of the researches*

Two companies out of three investigated ones are social active; however there are problems of strategic and management character with the CSR and management of CSR at the enterprise. Companies JSC «Zhytomyr Integrated Bakery», LLC «Organic Milk», and JSC «Beer-Alcohol-Free and Plant «Radomyshl'» have approximately equal level of social activities, however it is low and the corporate social responsibility remains on the initial level.

Such companies should direct their activities for the CSR development, namely:

1. To reach the second level. To increase the level of business reputation it is necessary to provide charities, sponsoring for educational institutions, health protection institutions, social establishments, and such stratums of population and organizations that need these actions within their possibilities;
2. To reach the third level. This is the level of the company responsibility before internal and external stakeholders. This level is characterized by increasing the level of responsibility before the interested parties. For internal stakeholders, it is the protection of owners' and investors' interests, observance of anti-corruption legislation. For personnel, the level provides the creation of additional social guarantees, social package, creation of corporate pension schemes, and organization of boarding, recreation, lodging, and medical service. The improvement of organization and culture of production in the direction of implementing international standards into the activities of the enterprise. The development of the system of internal firm programmes for training and re-training personnel, the establishment of corporate universities, and other departmental educational and health protection institutions etc. The implementation of «green office» programmes. For external stakeholders, it is the development of an honest business practice, collaboration with local communities and authorities, the development of stakeholders' map and realization of social responsible marketing etc. The public reporting about social activities and placing the results on the company site and in mass media;
3. To reach the fourth level (the level of the CSR strategic direction and social investments). The implementation and observance of national and European CSR standards. The development of strategy for social responsible actions and its integration into the company development strategy. Inclusion in the company development strategic map. The CSR principles are integrated into a mission, a strategy, a corporate culture. The mechanisms for strategic social investments are developed; the selection of the social projects closer to the company business is taken place. This level of development provides the building of the purposeful long-term programme of the company socio-economic and ecological policy within the area of its activities aimed at the solution of socially important targets, participation in public-private partnership programmes, transition to purpose-oriented social investments on both national and regional levels (Stverkova, Pohludka, Kurowska-Pysz, Szczepańska-Woszczyna, 2018; Meyer, Molefe, De Jongh, 2018) [32, 33]. Participation in solving urgent issues on the state level (poverty alleviation, the development of education, decreasing the unemployment level, the solution the problems concerning security etc.).

Conclusion

Thus there has been improved the methodology for the determination of the CSR efficiency integral index by using the system of qualitative and quantitative parameters of the CSR assessment, which unlike the existing ones, takes into account the indices of the internal and external CSR form and corresponds to the stakeholders' theory. The authors focus on

the significance of determination of the integral index which would take into account the indices by the directions of corporate activities, meet the consumers' needs, and first of all the needs of stakeholders, and also include the indices by such three principal components as economic, social, and ecological according to the principles of providing sustainable development. The value of the integral index allows determining the level of the company CSR development and can be used for building the ratings of socially responsible companies.

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Sectoral features in the formation of food industry enterprises competitiveness: case of Ukraine

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Abstract

Introduction. The purpose of research is to determine the main factors that influence on competitiveness of Ukrainian enterprises of various food sectors and assess their impact on the formation of competitive advantages.

Materials and methods. The analysis of scientific publications allowed to determine the most effective methods: a contextual comparative analysis to identify the force of influence on the competitiveness of Ukrainian food industry enterprises and expert method assessment.

Results and discussion. The main factors that reduce the competitiveness of Ukrainian food industry enterprises are: oligopolization of markets, high level of shadow sector, outdated technical level and technologies, low level of innovation activities, raw materials shortage and underdeveloped raw material sector, dependence on imported raw materials, weak logistics infrastructure, reduction of purchasing power, political and economic instability.

The most important factors that have a positive impact on the competitiveness of food industry enterprises and the formation of competitive advantages are: affiliation of food industry enterprises to transnational corporations, innovation activities and manufacturing modernization, compliance of products with international standards, deep recycling of raw materials, production of ecological products.

Ways of developing the competitive advantages are: rapid adaptation to changes, improving the efficiency production processes, taking into account the industry specifics and peculiarities of doing business, implementation of environmental standards in manufacturing. The force of factors that influence on the competitiveness of enterprises is different due to sectoral features of functioning.

Conclusion. The proposed approach allows to predict changes in the level of competitiveness, taking into account the industry specifics of the enterprise activity and changes of external environment, including changes in a particular commodity market.

Introduction

Enterprise competitiveness in current conditions is one of the defining characteristics of the efficiency of its economic activity and at the same time opportunities for further development.

According to Michael Porter, an American economist who is recognized as a specialist in the study of economic competition, competitiveness is the ability of a product, service, market entity to act on the market on a par with similar products, services, or competing market entities (Porter, 1990) [1]. However, selecting the price leadership strategy, differentiation or concentration, it is necessary to focus the attention on the development level of a certain enterprise, market factors, industry specifics and future growth opportunities.

Paul Krugman revived Adam Smith's idea that the size of the company is very important. He notes that often the efficiency of production directly depends on its size. As a result, goods produced at large enterprises in industrial countries, despite the much higher cost of labor, are cheaper than the same products in less developed countries (Krugman, 1996) [2]. At the same time, the majority of production plants are located in regions with cheaper labor force and other factors of production, ensuring constant control of quality indicators of finished products. Enterprise location choice in highly developed countries or in less developed countries remains a discussion issue.

C. Prahalad and G. Hamel emphasized that the competitiveness of an enterprise is based on "key competences", being a set of necessary skills. Due to them, an enterprise may gain specific benefits which translate into long-term advantage and, as a consequence, competitive position on the market (Hamel, Prahalad, 1996) [3]. However, it is advisable to consider the development of a competitive positioning and the factors influencing the competitive advantages.

Modern researchers prove that competitiveness is ensured at different levels. Thus, competitiveness can be found to describe processes of the globalising economy for companies (micro level), industrial sectors and regions (meso level) as well as for national economies (macro level). Thus, considering the pyramid model of competitiveness, it is crucial to examine all its levels in the system of competitive relations (product competitiveness – enterprise competitiveness – industry competitiveness – economic competitiveness – economic leadership) (Banwet, Momaya, Shee, 2002; Siudek T, Zawojska A., 2014; Bhawsar, Chattopadhyay, 2015; Tyunyukova, Ruban, Burovtsev, 2018; Vlados, Katimertzopoulos, 2018; Vlados, Chatzinikolaou, 2020)[4 – 9]. But the unresolved issue is the investigation of sectoral features of food processing enterprises and factors that form their competitiveness.

The purpose of research – to determine the main factors that justify the competitiveness of Ukrainian enterprises of various food industries at the meso level and assess their impact on the formation of competitive advantages and disadvantages.

Materials and methods

Object and subject of study

Object of study is the process of identifying the factors that influence on competitiveness of Ukrainian enterprises of various food sectors in modern market conditions.

Subject of study is a methodology and applied aspects of competitiveness of Ukrainian enterprises of various food industry sectors.

Research methods of enterprises competitiveness

The authors proposed a methodology to assess the impact of main factors on competitiveness of Ukrainian enterprises of various food industry sectors. Conducted macroeconomic analysis allowed to determine the main factors and assess their impact on competitiveness of Ukrainian food processing enterprises and propose ways of creating and developing the competitive advantages.

For this reason, in the research paper we'll focus on the analysis and assessment of factors that determine the level of competitiveness of enterprises operating in various sectors of Ukrainian food industry.

The theoretical basis for writing of this research paper was a set of general-scientific and special methods, based on modern approaches of economic theory and management theory:

- Scientific induction and deduction – in substantiation of the essential characteristics and clarification of the concept of "competitiveness" in modern conditions (Lawson, 2005) [10];
- Historical generalization and logical – to study the evolution of the concept of competitiveness, competitive advantages and their components (Guenther, Falk, 2019) [11];
- Abstract-logic – for theoretical generalization and formation of conclusions (Patkar, 2018) [12];
- Analytic groups – for systematization and classification of factors influencing the level of competitiveness and identification of consistent patterns of their influence on the final results of economic activity (Ibrahim, 2015) [13];
- Comparison and synthesis – to reveal the direction of influence of the main factors on the development of enterprises competitiveness (Shemilt, Mugford, Vale, Marsh, Donaldson, Drummond, 2010)[14];
- Expert assessment – to determine the force of influence of certain factors on the competitiveness of enterprises operating in various sectors of Ukrainian food industry (Karasev, Mukanina, 2019) [15].

Factors evaluation technique to justify the competitiveness of enterprises of various food industries

Comparative analysis was applied to investigate the factors influencing the competitiveness of various food industry enterprises (Pickvance, 2001) [16]. The initial data for conducting a contextual analysis are obtained from the publications of the results of scientific research of scientists, own research, as well as empirical data on the activities of food industry enterprises in the domestic market.

Factors that have negative impact and cause the formation of competitive disadvantages (competitive weaknesses) are: oligopolization of markets, increasing level of competition with foreign companies and goods, penetration of foreign producers into the market (including plant location), import of similar goods growth, dependence on foreign raw materials, dependence on imported technology and equipment, high level of shadow sector, higher competition in the domestic market, raw materials shortage and underdeveloped domestic raw material sector, outdated technical level, using outdated technologies, insufficient inter-industry relations, shortage of working capital for raw material procurement, unable to obtain affordable credit, reduction of purchasing power

Factors that have positive impact and cause the formation of competitive advantages (competitive strength) are: affiliation of food industry enterprises to transnational corporations, creation of different types of integrated structures, manufacturing modernization (including foreign investments), innovation activities, market growth, culture of consumption, stable financial performance and high enterprise rating activity, favourable trade conditions in international markets, product compliance with international standards, utilization of recycled and waste materials, deep recycling of raw materials, availability of highly qualified personnel, government support, stable markets for promotion of goods, production of ecological products.

Research methods to evaluate the force of factors affecting competitiveness

The necessity to determine the influence of forces of the main factors that confirm the enterprises competitiveness of various sectors of food industry has led to the use of expert assessment method. We conducted questioning with bringing of highly skilled employees from different departments of enterprises in various sectors of food industry. The survey was conducted on-line. The experts were presented with the list of factors to estimate the degree of influence of a certain factor on the competitiveness of enterprises of various sectors of food industry. It was proposed to evaluate the impact of each factor on the competitiveness of enterprises of various sectors of food industry:

- "+++" – a factor has a very significant impact;
- "++" – a factor has a significant impact;
- "+" – a factor has a non significant impact;
- "-" – a factor does not affect;
- "*" – the impact of the factor is not defined.

Due to the research results, main factors are determined and proved their force of influence on the enterprises competitiveness of various sectors of food industry in the strategic perspective.

Results and discussion

Critical analysis of modern approaches to the theory of competitiveness

It is crucial to consider the pyramid model of competitiveness in detail and examine all its levels (product competitiveness – enterprise competitiveness – industry competitiveness – economic competitiveness – economic leadership).

Competitiveness of the goods (products) is their degree of compliance with the requirements of a target audience of consumers or the selected market for the most important characteristics: technical, economic, environmental, etc. Competitiveness of a product is a combination of its consumer properties, which ensure its success in the market in comparison with similar products of other companies (Banwet, Momaya, Shee, 2002) [4].

Competitiveness of the product is determined by the following main factors (Tyunyukova, Ruban, Burovtsev, 2018) [7]: price, quality, level of after-sales service, advertising efficiency, system marketing, timing and production technology, sales volume.

Enterprise competitiveness is the level of its competence in relation to other competing companies in accumulating and using potential of its individual components: technology, resources, management (especially strategic current planning), staff skills and knowledge, etc. for product quality improving, boosting productivity and increasing profitability.

Enterprise competitiveness is the ability to use its strengths and concentrate its efforts in that sphere of production of goods or services where it can take an offensive position in markets (Bhawsar, Chattopadhyay, 2015; Vlados, Katimertzopoulos, 2018) [6, 8].

The main factors that determine the competitiveness of an enterprise include: company strategy, availability of materials, labor and financial resources, innovation potential, market share, management efficiency.

Industry competitiveness is reflected the enhancing firms' capabilities (through new or expanded technology, new methods) to offer better products and services, to produce products and services more efficiently, and/or to enter into new products and services (diversification) (Vlados, Chatzinikolaou, 2020) [9]. High competitiveness of enterprises which is illustrated in specific indicators provide the industry competitiveness.

Competitiveness at the national level (economic competitiveness) is based on superior productivity performance and the economy's ability to shift output to high productivity activities which in turn can generate high levels of real wages. Competitiveness is associated with rising living standards, expanding employment opportunities, and the ability of a nation to maintain its international obligations (GC, 1985) [17].

An economy is competitive if its population can enjoy high and rising standards of living and high employment on a sustainable basis (ECR, 2000) [18]. Economic leadership is the highest level of competitiveness which is characterized by an index of Gross National *Happiness* (to *measure* the collective *happiness* and well-being of a population) and key indicators of economic development (Verma, 2017) [19].

Review of the modern scientific research (Siudek, Zawojska, 2014; Vlados, Katimertzopoulos, 2018; Vlados, Chatzinikolaou, 2020; Balkyte, Tvaronavičiene, 2010; Momaya, 2011;) [5, 8, 9, 20, 21], made by authors, showed the enormous number of approaches to the theory of competitiveness.

From authors' point of view, enterprise competitiveness is the ability to compete and achieve high performance in certain activities accumulating and developing competitive advantages.

Main factors influencing the competitiveness of enterprises

It should be noted that we considered the level of enterprises competitiveness and industry competitiveness accordingly. The authors' research confirms that enterprise competitiveness shows the differences of one enterprise from its competitors in satisfying the customers' needs, as well as in the efficiency of production and economic activities. The concept of value chain is one of the tools for determining the enterprise competitiveness (Mostenska, Tur, 2018) [22]. It is also crucial to make an assessment of the competitive strength and company's competitive position. Accordingly, enterprise competitiveness is its ability to successfully compete in the market and receive economic benefits relative to competitors.

Main factors that affect the level of competitiveness of the enterprise are the following (Biukšāne, 2016; Okunevičiūtė Neverauskienė, Danilevičienė, Tvaronavičienė, 2020) [23, 24]:

- Technical and technological – factors characterizing production equipment, objects of labor, technology in the workplace. This group of factors is largely decisive, because the level of mechanization and automation of production, modern technologies implementation directly affect the operational efficiency of the enterprise;

- Organizational and management group contains factors that drive the technical and technological subsystem due to the organization of production and labor, staff selection, the introduction of a progressive wage system;
- Financial and economic factors deal with effective resource management, profitability and financial stability;
- Socio-psychological factors cover the staff of the enterprise, organizational culture, values, needs and interests of employees. It is necessary to maintain a healthy moral and psychological climate in the team, create normal working and resting conditions for the development of needs for self-actualization;
- Natural-geographical group of factors force the company to build its logistics structure, constantly improve production technology, optimize transportation schemes, reduce the energy intensity of production, etc.;
- Environmental group of factors consists of a whole complex of technical and organizational tasks due to the necessity of improving the quality of water, air, land, etc. To obtain a high competitive status;
- Industry group of factors reflects the external conditions of the business entity operating, identifying the ways of technology improvement, organization and production management at enterprises;
- Market factors include the open access to resources and new technologies, the product uniqueness, expending distribution channels and the effectiveness of sales promotion tools.

Competitive advantages investigation and their classification

From authors' point of view, the purpose of a business enterprise is to minimize costs and maximize profit for achieving its sustainable development. This proves that the management of the company should have a development strategy (business expansion, innovation, organizational change) for increasing profitability and development of competitive advantages and competitiveness as a whole.

A competitive advantage is an advantage over competitors gained by offering consumers greater value, either by means of lower prices or by providing greater benefits and service that justifies higher prices (Barney, 1995) [25]. *Competitive advantage* means superior performance relative to other competitors in the same industry or superior performance relative to the industry average.

From our perspective, competitive advantages are the collection of some strong prevailing characteristics of the company that clearly distinguish it from the competitors, providing further development through the production of high quality products and satisfying the growing needs of the consumers.

There is no one way to define the term "competitive advantage" and measure it. Nearly everything can be considered as competitive edge, e.g. higher profit margin, greater return on assets, valuable resource such as brand reputation or unique competence in producing jet engines. Every company must have at least one advantage to successfully compete in the market. If a company can't identify one or just doesn't possess it, competitors soon outperform it and force the business to leave the market (Thompson, Peteraf, Gamble, Strickland, Jain, 2013) [26].

The main types of competitive advantages are: (Kaleka, Morgan, 2017; Ma, 2000) [27, 28]:

- Resource: availability of resource access (price and quality of raw materials, remoteness of raw material zone), long-term collaboration with producers of raw materials;

- Technological: production capacity, availablility of modern equipment that affects the productivity and quality of finished goods, working processes optimization, patented technologies;
- Intellectual: highly skilled staff, optimal management system, innovation in tackling problems, research skills;
- Market: wide and large distribution network, exporting products, effective sales and after-sales service;
- Innovation: possibility to develop new products, implementation of new methods of production;
- Cultural: cross-cultural differences, product adaptation strategy.

Companies should develop their competitive advantages to have a high competitive position, attract new consumers and satisfy the needs of existing clients.

Assessment tools used by enterprises to improve the competitiveness

An organization can achieve an edge over its competitors in the following two ways: through external changes (a PESTEL analysis) and through internal opportunities (developing VRIO resources). PESTEL is an acronym for political, economic, social, technological, environmental and legal factors. It's a way of understanding how external forces impact your business. PEST analysis was created by Harvard professor Francis Aguilar in 1967 (Aguilar, 1967) [29]. When these factors change many opportunities arise that can be exploited by an organization to achieve superiority over its rivals. Changes in consumer demand, such as trend for eating more healthy food, can be used to gain at least temporary differentiation advantage if a company would opt to sell mainly healthy food products while competitors wouldn't. A company can also gain an upper hand over its competitors when it's capable to respond to external changes faster than other organizations. Otherwise, if a company is slow to respond to changes it may never benefit from the arising opportunities (Touati, 2013) [30].

Also, from authors' point of view to develop the enterprise competitiveness and competitive advantages it is necessary to take into account its own attributes. An enterprise can gain cost or differentiation advantage when it develops VRIO resources, unique competences or through innovative processes and products.

A company that possesses VRIO (valuable, rare, hard to imitate and organized) resources has an edge over its competitors due to superiority of such resources (Cardeal, António, 2012) [31]. If one company has gained VRIO resource, no other company can acquire it (at least temporarily). The following resources have VRIO attributes**:**

1. Intellectual property (patents, copyrights, trademarks)
2. Brand equity
3. Culture
4. Know-how
5. Reputation

All these attributes enhance the competitive advantages of the enterprise and facilitate its improvement and development. Many products can be identified by trademarks. Brand loyalty forms enterprise loyalty and that's crucial factor in competition (Kwan Soo Shin, Amenuvor, Basilisco, Owusu-Antwi, 2019) [32].

Brand equity is the real value for each enterprise because it provides added value (guarantee) to the clients that the product is unique (customized) and has specific (cannot be copied by competitors) characteristics. Brand image is what comes to people's mind when

they think of specific brand. Perceived value is formed through emotion, connection and feeling (He, José Manuel Guaita-Martínez, Botella-Carrubi, 2019) [33].

Culture reflects climate and morale spirit in the company, the ability to manage their people effectively relying on trust and relationship in people management. This allows to make right decisions about which people to hire (innovative productive employees) and the best way to use their skills (Zhao, HaimengTeng, QiangWu, 2018) [34]. Know-how is an approach about knowledge of how to do something and experience in doing it. High qualified staff with innovative view to business processes enrich the company by generation of creative ideas about future development (Purc, Laguna, 2019) [35].

Reputation is perception of the company and its brands. Strong brands, perfect experience in leading business operations create a positive reputation of the enterprise. Businesses with a good reputation make greater profits. Consumers respond to the reputation is reflected by making buying decisions for or against the company (Chun, Argandoña, Choirat, Siegel, 2019) [36].

Availability of these VRIO attributes provides a sustainable competitive advantage and increases the competitiveness of enterprises in the market. In further research it is possible to apply this methodology to study the competitiveness of a particular enterprise.

Study of the effectiveness of food industry development and their impact on the Ukrainian economy

In Ukraine, as well as all over the world, complex socio-economic and political processes are taking place, which form the conditions for the development of the Ukrainian food industry, which in the global dimension is part of the world food market. In this market, Ukrainian producers traditionally have high positions.

Economic competitiveness depends on industry competitiveness and enterprises competitiveness. In 2019, mining and processing industries of Ukraine provided more than 16% of GDP according to the State Statistics Service of Ukraine. The key place among all activities in the industry belongs to the processing industry, namely the production of foodstuffs, beverages and tobacco products. In 2019, the sales volume amounted UAH 530,5 bln. or 21,4% of total industrial volume [37].

The index of industrial production analysis by types of activity showed that only the processing industry retains 3-4% average annual growth from 2016. From 2015 to 2019, the relative stability and upward trend has been maintained only by short-term and long-term consumer goods (Table 1) [37].

The study of industrial production sales by types of activity by Ukrainian enterprises reflects positive trends in sales volumes (Table 2 and Table 3) [37].

Table 1

Indices of Industrial Production, by types of activity and main industrial groupings (percent over the previous period)

Industry and sectors	Code of CTEA-2010	2016/ 2015	2017/ 2016	2018/ 2017	2019/ 2018
Industry	B+C+D	104,0	101,1	103,0	99,5
Mining and manufacturing	B+C	104,1	102,4	103,0	100,2
Manufacturing	C	105,6	105,2	102,9	100,9
Production of foodstuffs, beverages and tobacco products	10–12	107,4	106,3	98,7	103,3
Manufacture of food products	10	108,9	107,1	98,5	103,9
Processing and preserving of meat and production of meat products	10.1	104,1	104,3	99,9	102,0
Processing and preserving of fish, crustaceans and molluscs	10.2	128,4	109,2	114,1	104,0
Processing and preserving of fruit and vegetables	10.3	106,0	101,6	109,9	99,4
Manufacture of vegetable and animal oils and fats	10.4	118,4	117,5	97,9	113,7
Manufacture of dairy products	10.5	99,7	100,8	101,7	95,1
Manufacture of grain mill products, starches and starch products	10.6	103,1	98,9	89,2	104,1
Manufacture of bakery and farinaceous products	10.7	97,6	98,5	95,0	94,0
Manufacture of other food products	10.8	111,3	102,2	98,3	93,4
Manufacture of sugar	10.81	133,6	100,9	89,6	82,8
Manufacture of cocoa, chocolate and sugar confectionery	10.82	97,2	106,5	107,7	111,3
Processing of tea and coffee	10.83	103,6	95,1	104,0	97,3
Manufacture of condiments and seasonings	10.84	100,8	103,3	100,0	101,6
Manufacture of other food products n.e.c.	10.89	93,8	102,3	104,9	64,1
Manufacture of beverages	11	96,3	100,8	100,8	99,7
Distilling, rectifying and blending of spirits	11.01	86,4	88,7	93,3	95,6
Manufacture of wine from grape	11.02	103,5	97,2	88,0	85,6
Manufacture of soft drinks; production of mineral waters and other bottled waters	11.07	105,6	114,9	111,2	107,7
Manufacture of tobacco products	12	102,2	95,3	91,4	87,6

[1]data exclude the temporarily occupied territory of the Autonomous Republic of Crimea, the city of Sevastopol and a part of temporarily occupied territories in the Donetsk and Luhansk regions
Source: authors' calculations based on data [37]

Table 2

Volume of industrial products sold by Ukrainian enterprises, by types of activity in 2016-2019[1] Mln.UAH, excluding VAT and excise

Industry and sectors	Code of CTEA-2010	Years				Rate of change		
		2016	2017	2018	2019	2017/ 2016	2018/ 2017	2019/ 2018
Industry	B+C+D+E	1767093,3	2153031,3	2508579,5	2480804,2	121,8	116,5	98,9
Mining and manufacturing	B+C	1367751,0	1714038,8	2017721,1	1992299,0	125,3	117,7	98,7
Manufacturing	C	1137784,9	1400214,0	1636893,0	1597451,8	123,1	116,9	97,6
Production of foodstuffs, beverages and tobacco products	10–12	381445,1	451114,8	504332,4	530505,1	118,3	111,8	105,2
Manufacture of food products	10	323898,9	380695,6	422730,5	443176,2	117,5	111,0	104,8
Processing and preserving of meat and production of meat products	10.1	50692,4	62921,8	75160,6	76495,0	124,1	119,5	101,8
Processing and preserving of fish, crustaceans and molluscs	10.2	2997,1	3782,2	4853,6	5681,1	126,2	128,3	117,0
Processing and preserving of fruit and vegetables	10.3	11267,5	13142,5	15680,6	18425,6	116,6	119,3	117,5
Manufacture of vegetable and animal oils and fats	10.4	106563,0	124812,0	132746,4	133365,2	117,1	106,4	100,5
Manufacture of oils and fats	10.41	99154,4	115350,0	124203,9	127851,0	116,3	107,7	102,9
Manufacture of dairy products	10.5	39972,1	51561,5	57638,6	60637,9	129,0	111,8	105,2
Manufacture of grain mill products, starches and starch products	10.6	14601,3	16348,6	17402,0	19160,3	112,0	106,4	110,1
Manufacture of grain mill products	10.61	10935,7	11777,1	12997,2	14132,6	107,7	110,4	108,7
Manufacture of bakery and farinaceous products	10.7	27307,0	30698,6	33733,7	37543,9	112,4	109,9	111,3
Manufacture of bread; manufacture of fresh pastry goods and cakes	10.71	14917,2	17098,5	18840,5	20898,1	114,6	110,2	110,9

Table 2 ***(continue)***

Industry and sectors	Code of CTEA-2010	Years				Rate of change		
		2016	2017	2018	2019	2017/ 2016	2018/ 2017	2019/ 2018
Manufacture of macaroni, noodles, couscous and similar farinaceous products	10.73	696,9	660,3	796,8	1282,7	94,7	120,7	161,0
Manufacture of other food products	10.8	56632,3	61588,1	66260,7	68090,0	108,8	107,6	102,8
Manufacture of sugar	10.81	18488,7	17907,5	15156,5	12232,6	96,9	84,6	80,7
Manufacture of cocoa, chocolate and sugar confectionery	10.82	15539,1	18255,6	21087,0	22472,0	117,5	115,5	106,6
Processing of tea and coffee	10.83	5287,2	5019,7	5196,5	8550,0	94,9	103,5	164,5
Manufacture of condiments and seasonings	10.84	5739,9	7124,2	8562,2	8889,4	124,1	120,2	103,8
Manufacture of prepared meals and dishes	10.85	2531,4	3513,3	4560,4	5260,2	138,8	129,8	115,3
Manufacture of other food products n.e.c.	10.89	8371,2	8998,0	10851,1	9737,4	107,5	120,6	89,7
Manufacture of beverages	11	40856,3	46902,4	55394,0	61100,8	114,8	118,1	110,3
Distilling, rectifying and blending of spirits	11.01	8822,9	9126,7	10433,0	11361,2	103,4	114,3	108,9
Manufacture of wine from grape	11.02	4312,5	4639,0	4852,3	3518,1	107,6	104,6	72,5
Manufacture of beer	11.05	14354,2	17369,5	20546,4	23835,7	121,0	118,3	116,0
Manufacture of soft drinks; production of mineral waters and other bottled waters	11.07	11010,8	13183,6	16740,8	19164,5	119,7	127,0	114,5
Manufacture of tobacco products	12	16689,9	23516,8	26207,9	26228,1	140,9	111,4	100,1

[1] Data exclude the temporarily occupied territory of the Autonomous Republic of Crimea, the city of Sevastopol and temporarily occupied territories in the Donetsk and Luhansk regions.
Source: authors' calculations based on data [37]

Table 3

Volume of industrial products sold outside Ukraine, by types of activity in 2016-2019[1], Mln.UAH, excluding VAT and excise

Industry and sectors	Code of CTEA-2010	Years				Rate of change		
		2016	2017	2018	2019	2017/ 2016	2018/ 2017	2019/ 2018
Industry	B+C+D+E	466752,4	596313,0	682022,3	649212,1	127,8	114,4	95,2
Mining and manufacturing	B+C	465542,7	594867,8	679378,1	647175,9	127,8	114,2	95,3
Manufacturing	C	408473,3	517745,5	594272,4	549451,3	126,8	114,8	92,5
Production of foodstuffs, beverages and tobacco products	10–12	91382,9	122003,2	135342,8	139314,8	133,5	110,9	102,9
Manufacture of food products	10	81741,8	110019,8	121572,6	125572,3	134,6	110,5	103,3
Processing and preserving of meat and production of meat products	10.1	597,1	1127,2	2205,4	1790,7	188,8	195,7	81,2
Processing and preserving of fish, crustaceans and molluscs	10.2	511,5	972,1	509,9	282,9	190,0	52,5	55,5
Processing and preserving of fruit and vegetables	10.3	2885,3	3668,7	3910,7	4191,9	127,2	106,6	107,2
Manufacture of vegetable and animal oils and fats	10.4	59441,8	79628,6	88918,4	93133,7	134,0	111,7	104,7
Manufacture of oils and fats	10.41	58721,3	78405,9	87909,0	92601,2	133,5	112,1	105,3
Manufacture of dairy products	10.5	2413,7	4253,9	4285,6	3841,0	176,2	100,7	89,6
Manufacture of grain mill products, starches and starch products	10.6	2845,1	3681,2	3575,3	4742,4	129,4	97,1	132,6
Manufacture of grain mill products	10.61	1829,0	2192,6	2099,7	2743,2	119,9	95,8	130,6
Manufacture of bakery and farinaceous products	10.7	2615,0	3080,5	4019,9	4207,4	117,8	130,5	104,7
Manufacture of bread; manufacture of fresh pastry goods and cakes	10.71	358,0	177,0	152,3	167,1	49,4	86,0	109,7

Table 3 ***(continue)***

Industry and sectors	Code of CTEA-2010	Years				Rate of change		
		2016	2017	2018	2019	2017/ 2016	2018/ 2017	2019/ 2018
Manufacture of rusks and biscuits; manufacture of preserved pastry goods and cakes	10.72	2233,8	2890,1	3850,6	3929,0	129,4	133,2	102,0
Manufacture of macaroni, noodles, couscous and similar farinaceous products	10.73	23,2	13,4	17,0	111,3	57,8	126,9	654,7
Manufacture of other food products	10.8	10118,7	13188,3	13691,6	12988,8	130,3	103,8	94,9
Manufacture of sugar	10.81	1141,5	2082,5	1691,0	896,6	182,4	81,2	53,0
Manufacture of cocoa, chocolate and sugar confectionery	10.82	5030,0	6003,3	6427,1	6911,5	119,3	107,1	107,5
Processing of tea and coffee	10.83	137,3	261,4	270,4	s	190,4	103,4	-
Manufacture of condiments and seasonings	10.84	620,1	776,0	920,0	977,2	125,1	118,6	106,2
Manufacture of prepared meals and dishes	10.85	634,4	802,7	941,8	970,6	126,5	117,3	103,1
Manufacture of other food products n.e.c.	10.89	2549,2	3251,3	3432,5	2520,8	127,5	105,6	73,4
Manufacture of beverages	11	2428,8	3184,7	3519,9	2834,6	131,1	110,5	80,5
Distilling, rectifying and blending of spirits	11.01	1053,1	1144,8	1366,0	1334,4	108,7	119,3	97,7
Manufacture of wine from grape	11.02	419,9	754,3	649,5	79,8	179,6	86,1	12,3
Manufacture of beer	11.05	427,2	726,3	836,2	878,7	170,0	115,1	105,1
Manufacture of soft drinks; production of mineral waters and other bottled waters	11.07	131,6	147,8	272,3	198,9	112,3	184,2	73,0
Manufacture of tobacco products	12	7212,3	8798,7	10250,3	10907,9	122,0	116,5	106,4

[1] Data exclude the temporarily occupied territory of the Autonomous Republic of Crimea, the city of Sevastopol and temporarily occupied territories in the Donetsk and Luhansk regions.
Source: authors' calculations based on data [37]

At the same time, having unconditional success in modernizing the technology of production, improving its quality and expanding the range, Ukrainian food industry enterprises have not yet entered the trajectory of sustainable development. Ukraine is experiencing a decline in the level of food production, rising prices for raw materials, insufficient level of interaction between producers of raw materials and producers of the final product (Pimenova, Fyliuk, Pimenov, 2020; Galunets, 2019) [38, 39].

Analysis of the factors influencing the competitiveness of food processing enterprises

In the authors' opinion, investigating the factors which determine the competitive environment of Ukrainian food industry enterprises (political, economic socio-cultural, technological, legal), it is crucial to add environmental factors because they influence much on the competitiveness and increase the loyalty of consumers to the companies:

- Political factors. Functioning of enterprises depend on the laws and regulations of the country (lobbying of interests**,** increase or decrease in taxes**,** bureaucracy, corruption level, competition regulation, government stability and related changes, government involvement in trade unions and agreements, import restrictions on quality and quantity of product, etc.).
- Economic factors are connected with goods, services, and money (inflation, interest rates, exchange rates, consumers' income and purchasing power, economic growth and unemployment) (Cepel, Belas, Rozsa, Strnad, 2019) [40].
- Socio-cultural factors are the larger scale forces within cultures and societies that affect the thoughts, feelings and behaviors (cross-cultural differences, regional differences, religious beliefs, attitudes, etc.) (Bartelsman, Haltiwanger, Scarpetta, 2013) [41].
- Technological factors refer to the ways new practices and equipment can affect businesses (information communication technology, automation, e-commerce, etc.) (Andersson, Hellsmark, Sandén, 2018) [42].
- Legal factors are external factors which refer to how the law affects the way businesses operate and customers behave.
- Environmental factors. Enterprises should be eco-friendly and try to reduce consumption of resources (saving of natural resources, environmental protection, wastes utilization, alternative energy production, production of environmentally friendly food) (Ramón, 1994) [43].

The analysis of food industry competitiveness showed the heterogeneity of the situation in the industry markets. Own researches and expert assessment have shown that some factors have different force of influence on the enterprises competitiveness of different sectors of food industry. Such results should be taken into account determining the strategic priorities of enterprises development (Table 4).

Table 4

Main factors determining the level of competitiveness of enterprises functioning in the food industry

Factors of competitiveness	Sectors of food industry												
	Manufacture of tobacco products	Manufacture of beer	Manufacture of soft drinks; production of mineral waters and other bottled	Manufacture of cocoa, chocolate and sugar confectionery	Processing and preserving of fruit and vegetables	Processing and preserving of meat and production of meat products	Manufacture of dairy products	Manufacture of sugar	Manufacture of vegetable and animal oils and fats	Manufacture of grain mill products	Manufacture of bread; manufacture of fresh pastry goods and cakes	Manufacture of distilled spirits	Manufacturing of alcoholic beverages
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Negative impact (competitive disadvantages)													
Oligopolization of markets	+++	+++	+++	+++	+	++	++	-	+++	-	+/++	+++	+++
Increasing level of competition with foreign companies and goods	+++	+++	++	+++	+++	+/++	++	+	+	+	+	-	+++
Penetration of foreign producers into the market (including plant location)	+++	++	++	+	+	*	++	-	+++	-	-	-	+
Import of similar goods growth	+++	+++	+	+++	+++	++	++	+	+	+	+	-	++/+++
Dependence on foreign raw materials	+++	+++	++	++	*	++	+/++	+	-	-	+	-	-
Dependence on imported technology and equipment	+++	+++	++/+++	++/+++	++	++	++	+	++	+	+	-	++
High level of shadow sector	++	+++	++	++	+	++	-	-	-	-	+	+++	+++
Higher competition in the domestic market	+++	+++	++/+++	+++	++	++	+++	*	+/++	+/++	++	+	+++
Raw materials shortage and underdeveloped domestic raw material sector	+++	++	+	++	++	+++	+++	++	-	+	+	-	+
Outdated technical level	-	-	+	+	++	++	+	+++	-	++	++	+++	++

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Using outdated technologies	-	+	+	+/++	+++	+/++	+/++	+++	-	+++	++	+++	++
Insufficient inter-industry relations	+++	+++	+++	++	+++	++	++	+++	++	++	++	++	++
Shortage of working capital for raw material procurement	++	++	++	++	+++	+++	+++	+++	++	+++	+++	+++	++
Unable to obtain affordable credit	+	++	++	++	+++	+++	+++	+++	+	+++	+++	+++	++
Reduction of purchasing power	++	++	+++	+++	++	+++	+++	+	++	+++	+++	*	+
Existing competitive advantages													
Affiliation of food industry enterprises to transnational corporations	+++	+++	+++	+	-	++	++	-	+++	-	-	-	+
Creation of different types of integrated structures	+	++	++	+++	++	++	++	+	+++	++	+/++	++	++
Manufacturing modernization (including foreign investments)	+++	+++	+++	+++	++	++	++	-	+++	-	++	-	+
Innovation activities	+++	+++	++	++/+++	++	++	++	-/+	+++	+/++	++	-	+
Market growth	++	++	+++	+	++	++	++	+	+	++	+	++	++
Culture of consumption	+++	+++	++	+++	++	+++	+++	++	+++	+++	++	*	+++
Stable financial performance and high enterprise rating activity	+++	+++	+++	++	++	++	++	-	+++	+/++	++	+	++
Favourable trade conditions in international markets	+++	++/+++	++	+/++	*	+	+	+	+++	-	+	-	+/++
Product compliance with international standards	+++	+++	+++	+++	+	++	++	+	+++	+	++	++	+++
Utilization of recycled and waste materials	*	+	*	+	+	+	+	+	+++	+	+	+	*
Deep recycling of raw materials	++	+	*	+	+++	+++	+++	++	+++	++	++	++	*
Availability of highly qualified personnel	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++
Government support	-	-	-	-	-	-	+	-	-	++	++	++	-
Stable markets for promotion of goods	+++	++	++	++	++	++	++	++	++	++	++	+++	+++
Production of ecological products	-	-	++	++	++	++	++	+	++	++	++	-	-

Indication: "+++" – a factor has a very significant impact;
"++" – a factor has a significant impact;
"+" – a factor has a non significant impact;
"-" – a factor does not affect;
"*" – the impact of the factor is not defined.
Source: Authors' own research

Expert assessment and own research have proven that the specified factors can have both negative influence and cause the formation of competitive disadvantages (competitive weaknesses) and positive influence and prove the formation of competitive advantages (competitive strength).

On the basis of expert assessment it has been shown that the force of the influence of each factor on the enterprises competitiveness of various industries is different. According to the table 4, one factor may have a very significant impact or not affected on the formation of enterprises competitiveness in certain industries. So the dependence on foreign raw materials has a very strong influence on manufacture of tobacco products and beer and has a moderate influence on manufacture of soft drinks and cocoa, chocolate and sugar confectionery, while the enterprises of manufacturing the distilled spirits and alcoholic beverages are used Ukrainian raw materials. Among competitive advantages, we should mention that production of ecological products is the advantage of enterprises which produce soft drinks; mineral waters and other bottled waters, confectionery, canned fruits and vegetables, meat products, sugar, sunflower oil, flour and cereals, but for instance tobacco and alcohol products do not have such advantage. However, general environmental friendliness of production is an important competitive advantage for all enterprises of food industry.

The research has proved that different factors can both increase and decrease the level of competitiveness of Ukrainian enterprises in food markets.

Conducted macro analysis allowed to determine the main factors that prove the competitiveness of enterprises in various food industries.

Analyzing the changeable market environment, the main aspects which should be emphasized by modern mangers for future development of food industry enterprises are following:

- Higher efficiency (enterprises need to be efficient and try to cut costs in order to survive);
- Increasing quality of processes and products;
- Better material and ingredients usage and meeting higher standards (companies in food industry should always stick to the standards of health which means they should be care about ingredients which products consist with; also enterprises usually compete with the quality and nutritional value of the goods);
- Lower prices according to purchasing power;
- Greater output (companies will produce more goods and range of product to satisfy customers' needs and allow them to choose products);
- Rivalry among the companies and opportunities of the clients to switch on the substitute products (complication, sometimes impossibility to forecast and prognostication of competitors' actions);
- Seasonality and the culture of products consumption.

Conclusions

Thus, growth of competition on the market causes the necessity of improving the enterprise activity. Considering the possible ways of development of competitive advantages, it is necessary:

- To review the organizational structure in order to ensure better coordination of different departments;
- To understand and implement the procedures and rules in practical activity of the enterprise to achieve rationalization of processes;

- To ensure the possibility of rapid adaptation of the enterprise to changes in the external environment (innovative products, new customers' needs, market expansion, improvement of logistics processes, etc.);
- To implement the best management practices of other companies, taking into account the industry specifics and peculiarities of doing business (resource-saving technologies, improving the organization processes, methods of personnel management);
- To introduce the modern systems of product quality management, improve the technical control methods, implement the modern forms and methods of production.

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Анотації

Харчові технології

Фітохімічний склад ефірної олії наземних частин цмину піскового з Туреччини

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Вступ. Мета дослідження – визначити фітохімічний склад ефірної олії наземних частин цмину піскового (інша назва – безсмертник, *Helichrysum arenarium* (L.)), зібраного в Туреччині, та екстрактів як джерела біоактивних компонентів для харчової, косметичної й фармацевтичної промисловості.

Матеріали і методи. Ефірну олію з квіток отримували гідродистиляцією протягом 2 год. Склад олії аналізували за допомогою газохроматографічного аналізу (ГХ/МС). Екстракти отримували із сушених на повітрі квітів обробкою 70 та 90% етанолом (1:5 об/мас.) в ультразвуковій ванні. Загальний вміст фенолу в екстрактах визначали методом Фолін-Сікалтеу, вміст флавоноїдів – за допомогою реагентів $Al(NO_3)_3$, виміряних при довжині хвилі 415 нм. Антиоксидантну активність екстрактів визначали за допомогою аналізу DPPH, ABTS, FRAP та CUPRAC.

Результати і обговорення. Кількість видобутої ефірної олії становило 0,07% з основними складовими: олеїнова кислота (30,28%), етилгексадеканоат (20,19%), лінолева кислоти (18,89%) і склереол (4,22%). У складі олії переважають оксигеновані вуглеводні (76,90%), потім дитерпени (11,50%), вуглеводні (3,53%)), оксигеновані сесквітерпени (3,30%), феніл-пропаноїди (2,93%), сесквітерпенові вуглеводні (1,43%), монотерпенові вуглеводні (0,34%) та оксигеновані монотерпени (0,07%). Вміст загальних поліфенолів у 95% етанолових екстрактах становив 7,56 мг GAE/г сухих речовин, а загальних флавоноїдів – 3,13 mg GAE/г сухих речовин, тоді як їхній вміст у 70% етаноловому екстракті становив 6,62 мг і 3,34 мг GAE/g сухих речовин відповідно. Серед рослинних зразків 70-процентний етаноловий екстракт демонстрував вищий вміст CUPRAC (159,46 mM TE/g сухих речовин), з подальшим знебарвленням радикальної дії ABTS (mM TE/g сухих речовин). Результати для екстрактів етанолу та їхньої антиоксидантної активності відповідали загальному вмісту фенолу та концентрації флавоноїдів. У квітках переважали загальні каротиноїди (10,68 мкг/г сухих речовин) і загальний хлорофіл (51,24 мкг/г сухих речовин). Вміст хлорофілу a (32,67) був вищим, ніж вміст хлорофілу b (18,57 мкг/г сухих речовин).

Висновки. Основними сполуками ефірної олії цмину піскового були олеїнова кислота, етилгексадеканоат, лінолева кислота і скляреол. Екстракти показали високий рівень загального вмісту фенолу й антиоксидантного потенціалу, що робить досліджувані види рослин потенційним джерелом альтернативного природного антиоксиданту або джерелом біологічно активних компонентів.

Ключові слова: *цмин піщаний, безсмертник, Helichrysum arenarium L., ефірна олія, фенол, антиоксидант.*

Підвищення якості вторинної сировини від переробки сої фізичними методами при її використанні в технологіях хлібобулочних виробів. Огляд

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Вступ. Вторинна сировина від переробки сої (ВСПС) має високу харчову цінність, однак її застосування в їжі обмежується через смак і низький вміст розчинних харчових волокон.

Матеріал і методи. Предметом дослідження є властивості ВСПС, розчинні харчові волокна, інгібітор трипсину, фізичні методи обробки сировини, хлібобулочні вироби та випічка. Метод дослідження – аналіз і синтез інформації з провідних світових наукових публікацій.

Результати і обговорення. На основі аналізу результатів досліджень впливу фізичних факторів переробки ВСПС на їхню харчову цінність, технологічні та споживчі властивості готової продукції доведено актуальність та перспективність використання ВСПС у технології випічки. Високий тиск суттєво впливає на розчинні харчові волокна та функціональні властивості бобових відходів. Під дією високого тиску (400 МПа, 60 ℃) вміст розчинних харчових волокон збільшується у 8 разів при обробці ВСПС порівняно з необробленими. Покращуються властивості набухання та властивості утримання води (олії). ВСПС після ультратонкого помелу мають покращені технологічні властивості, а їх використання у випічці призводить до покращення її органолептичних показників. Ультратонкий помел покращує фізико-хімічні властивості ВСПС (в'язкість, катіонообмінна здатність, здатність утримувати воду і олію, розчинність, гідратаційні властивості, плинність, антиоксидантна активність), технологічні властивості (формувальність тесту, стабільність його структури), органолептичні показники. Завдяки мікрохвильовій обробці, яка має високу проникаючу здатність, підвищується тиск в клітинах матеріалу і відбувається його розширення та розрив. У результаті вміст розчинних харчових волокон у ВСПС збільшується. Мікрохвильова обробка є ефективним способом інактивації активності інгібітора протеази в тріщинах сої; обсмажування протягом лише двох хвилин знижує активність інгібітора трипсину до 13,33% від початкової.

Висновок. Використання комбінації фізичних методів для поліпшення якості ВСПС є перспективним. Ультратонкий помел має переваги порівняно з іншими фізичними методами та суттєво впливає на фізико-хімічні й технологічні властивості ВСПС, при цьому якість хлібобулочних виробів та випічки підвищується.

Ключові слова: *соя, відходи, волокна, хліб.*

Технологічні і хімічні аспекти зберігання та комплексної переробки насіння промислових конопель

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Вступ. Метою статті є теоретичні та експериментальні дослідження аспектів технології зберігання насіння промислових конопель, складу та якості продуктів його переробки.

Матеріали і методи. Матеріали дослідження – насіння промислових конопель сорту Гляна, пресова олія та конопляне ядро. Для дослідження показників складу і якості насіння промислових конопель при тривалому зберіганні (12 місяців) було підготовлено 12 поліпропіленових ємностей, наповнених вихідним насінням конопель після його первинної обробки.

Результати і обговорення. Виявлено, що вміст вологи у насінні становив 8,2–10,0 %; чистота насіння – 97,5–99,8%; вміст олії – 31,9–34,3%; маса 1000 насінин – 17,7–19,2 г; насипна маса насіння – 503,8–530 г/л. Встановлено зменшення вмісту олії у насінні в другій половині терміну зберігання. Вихід пресової фільтрованої олії збільшився в кінці терміну зберігання. Виявлено збільшення кислотного числа олії впродовж усього терміну зберігання насіння (0,91–1,46 мг КОН/г). Пероксидне число в першій половині терміну зберігання насіння конопель не перевищувало 5 ½ О ммоль/кг, а в другій збільшилось до 10 ½ О ммоль/кг. Основними ненасиченими жирними кислотами в дослідженій конопляній олії є олеїнова (14,9–19,4%), лінолева (53,4–56,6%), α-ліноленова (11,3–16,2%). Співвідношення есенціальних кислот ω-6 і ω-3 у досліджених зразках олії близьке до ідеального – 3,4:1–5,0:1. Вихід пресової макухи був 67,1–70,0% при вологості 6,6–9,0% та при вмісті олії 9,5–12,3%. Вихід фільтрувального осаду становив 4,6–8,6% при вологості 4,4–16,8% та при вмісті олії 49,2–64,4%. Вихід конопляного ядра – 33,2–41,4%; вміст у конопляному ядрі вологи – 6,9–7,8%, сторонніх домішок – 0,01–0,04%. Встановлено, що вміст олії в конопляному ядрі, отриманому з насіння української селекції сорту Гляна, збільшився на 5,9–8,5% порівняно з контролем.

Висновки. Обґрунтовано доцільність використання насіння промислових конопель сорту Гляна для раціональної переробки при стандартизації умов зберігання протягом річного терміну.

Ключові слова: *коноплі, насіння, зберігання, олія, ядро, функціональність.*

Вплив природних замінників цукру – мескітового борошна (*Prosopis alba*) та цукру кокосового горіха (*Cocos nucifera* L.) на якісні показники бісквітних коржів

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Вступ. Метою дослідження є оцінка фізико-хімічних і мікробіологічних характеристик бісквітних коржів із природними цукрозамінниками – борошном мескіту (Prosopis alba) та цукром кокосового горіха (Cocos nucifera L.).

Матеріали і методи. Бісквіт готували з пшеничного борошна, цукру, яєць з додаванням кокосового цукру та мескітового борошна у співвідношенні 3:1 як натуральних замінників цукру. Бісквіти зі 100% замінниками цукру обробляли при постійному режимі випікання одночасно з контрольним зразком.

Результати і обговорення. Питомий об'єм коржів коливався від 2,92±0,10 $см^3$/г до 3,13±0,11 $см^3$/г. У цьому дослідженні обсяг бісквіту із замінниками цукру був меншим, ніж об'єм контрольного коржа (219,00±2,07 $см^3$). Найбільша пористість спостерігалась у контрольному коржі (63,23±1,30%). Водопоглинальна здатність коржа з кокосовим цукром і мескітовим борошном (315,60±3,08%) є нижчою, ніж у контрольного. Втрати на випікання всіх зразків становили 15,27–17,55%. Коржі із цукрозамінниками мали менші втрати при випіканні і статистично відрізнялись від контролю. Корж контрольної проби мав найвищі значення L* (58,46±2,25), a* (9,56±0,62) і b* (25,31±0,82). М'якуш і колір скоринки коржа з кокосовим цукром і мескітовим борошном був коричневим і темнішим, ніж корж для контролю пирога та скоринки. Найвищий вміст жиру спостерігався в контрольному зразку (6,89%), а найнижчий – у коржі з кокосовим цукром і мескітовим борошном (5,66%).

Найвищий відсоток вуглеводів був у контрольному зразку – 58,21%, найнижчий – у коржі з кокосовим цукром і мескітовим борошном (23,50%). Важливо зазначити, що бісквіт з натуральними замінниками цукру може бути позначений як харчовий продукт з високим вмістом харчових волокон. Енергетична цінність коржа з кокосовим цукром і мескітовим борошном найнижча – 209,98 ккал/100 г продукту. З мікробіологічної точки зору, у перший день зберігання за кімнатної температури, на зразках не виявлено ознак патогенних бактерій та цвілі.

Висновки. Бісквіт, виготовлений з композиційного кокосового цукру та мескітового борошна має добрі технологічні характеристики. З функціональної та харчової точки зору ці коржі містять більше харчових волокон, ніж традиційні хлібні вироби з цукром.

Ключові слова: *корж, бісквіт, цукрозамінник, мескітове борошно, кокосовий горіх.*

Вплив плазмохімічно активованих водних розчинів на процес виробництва харчових проростків

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Вступ. Досліджено вплив плазмохімічно активованих водних розчинів на процес виробництва харчових проростків з бобових культур. У статті представлено характеристику активованих водних розчинів, визначено особливості їхнього впливу на процес проростання та мікробіологічний стан пророщеного матеріалу.

Матеріали і методи. Пророщували зерно бобових (горох, соя, нут, квасоля, сочевиця, боби, люпин) з використанням як інтенсифікатора проростання плазмохімічно активованих водних розчинів. Для визначення амінокислотного та вітамінного складу проростків було використано метод іонообмінної рідинно-колонної хроматографії.

Результати і обговорення. Енергія та здатність проростання у бобових підвищувалась при використанні плазмохімічно активованих водних розчинів. При оптимальній концентрації пероксидів 400 мг/л енергія проростання збільшилась на 10–12%, здатність до проростання – на 8–10%. Моніторинг довжини проростків показав, що довжина збільшилась від 6 до 14 мм. Контроль ваги біомаси проростків теж мав позитивні результати. Так, вага проростків підвищилась на 4–16 % залежно від культури (горох − 8%; соя − 10%; нут − 7%; квасоля − 14%; сочевиця − 4%; боби − 16%; люпин − 10%).

Дослідження мікробіологічного стану проростків показало сталу дезінфікуючу дію плазмохімічно активованих водних розчинів, обумовлену наявністю в їхньому складі перекису водню (100–700 мг/л). На проростках оброблених плазмохімічно активованими водними розчинами з концентрацією пероксидів 400 мг/л і більше не фіксувалась патогенна мікрофлора (Aspergillus, Alternaria, Penicillium, Fusarium, Mucor).

У проростках бобових при використанні плазмохімічно активованих водних розчинів підвищувався вміст вітамінів групи В (B_1, B_2, B_3, B_6, B_{12}), а також РР, Е, С, А. Кількість амінокислот збільшилась на 4–52%. Пояснюється це більш активним розвитком проростків бобових при використанні інтенсифікатора проростання − плазмохімічно активованих водних розчинів..

Висновки. Використання плазмохімічно активованих водних розчинів є перспективним технологічним прийомом отримання високоякісного продукту, багатого на амінокислоти та вітаміни.

Ключові слова: *проростки, активація, інтенсифікатор, проростання, бобові.*

Вплив несолодованого ячменю на виробництво слабоалкогольного та безалкогольного пива

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Вступ. Метою дослідження є обґрунтування виробництва слабоалкогольного і безалкогольного пива шляхом зміни складу сусла (заміна частини солоду несолодованим ячменем).

Матеріали і методи. Використовували промисловий солод і несолоджений ячмінь. Спиртове бродіння проводили з використанням вільного та альгінат-хітозанового капсульованого верхньоферментуючого штаму дріжджів *Saccharomyces cerevisiae* S-33. Режим затирання включав дві паузи – 30 хв при 50 ° С і 60 хв при 77 °С. Альдегіди визначали за методом бісульфіту, концентрацію складного ефіру – шляхом омилення складного ефіру NaOH. Метаболіти визначали після простої перегонки зразка пива.

Результати і обговорення. Екстракт сусла зменшувався із збільшенням кількості несолодженого ячменю. У вибраному процесі затирання цукри, що піддаються ферментації, коливались від 3,4 до 4,17% і становили близько 50% екстракту

лабораторного сусла. Використання 20% ячменю як допоміжного засобу призвело до зменшення екстракту сусла на 10%, але це несуттєво вплинуло на в'язкість. Основним недоліком використання несолодового ячменю є збільшення часу фільтрування лабораторного сусла. При 20-відсотковому вмісті допоміжного засобу час фільтрування становив 60–75 хв.

Було вирішено замінити 20% солоду несолодовим ячменем. У напівромислових умовах виготовлено сусло з таким кількісним співвідношенням солоду до ячменю: екстракт 8,03% мас. : вміст ферментованого цукру 3,7%). Отримане сусло піддавали спиртовому бродінню при 10 ° С протягом 7 днів із вільними та іммобілізованими клітинами, і для кожного варіанту визначали кінетику бродіння. Процес із вільними клітинами тривав відносно повільно і протягом перших 2–3 днів накопичувалось до 0,4% алкоголю, що відповідає швидкості бродіння 11%. Зміни відбулись у вторинному метаболізмі (збільшення виробництва ефірів, утворення вищих спиртів синтез слабких карбонільних сполук). В іммобілізованих клітинах початок бродіння також затримувався. Фактичний процес розпочався після четвертого дня, коли бродіння швидко досягло рівня вільного бродіння клітин. У результаті в лабораторному пиві накопичилося більше алкоголю (близько 0,7%), що дало змогу класифікувати його як слабоалкогольне пиво. У пиві накопичилося менше метаболітів, які в поєднанні з низькою температурою бродіння негативно вплинули на смаковий профіль.

Висновки. Технологічні режими виробництва слабоалкогольного і безалкогольного пива були обрані на основі аналізу цукрів сусла, а також на основі вивчення кінетики бродіння за низьких температур із вільними та іммобілізованими дріжджовими клітинами.

Ключові слова: *пиво безалкогольне, солод, ячмінь, бродіння.*

Вплив низькоглютенових зернових культур на властивості пива

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Вступ. Показано перспективність використання гречки і гречаного солоду для виробництва низькоглютенового пива.

Матеріали і методи. Пивне сусло та пиво виготовляли з обрушеної гречки білої (ОБГ) і гречаного солоду (ГС) у співвідношенні 85, 90, 95 відсотків ячмінного солоду (ЯС) і 15, 10, 5 відсотків (обрушеної гречки – ОБГ і гречаного солоду – ГС). Для визначення вмісту амінного азоту використовували йодометричний метод, для визначення вмісту редукуючих речовин – метод Вільштетера-Шудля, вміст білка визначали за методом Кельдаля, вмісту крохмалю – за методом Еверса.

Результати і обговорення. В таких злаках, як гречка та рис глютен відсутній, а в інших злаках кількість глютену складає: кукурудза – 80 ppm, ячмінь – 151 ppm, пшениця – 162 ppm. Тому для приготування низькоглютенового пива рекомендовано обрушену білу гречку, гречаний солод та ячмінний солод.

Зразок із заміною 5% ячмінного солоду на гречаний має найбільший вміст редукуючих речовин (91,0 г на 100 г екстракту) і амінного азоту (167,1 мг на 100 г екстракту). Вміст етилового спирту в готовому пиві 3,5 % масових при значенні масової частки дійсного екстракту 4,83% масових.

При заміні ячмінного солоду на обрушену білу гречку кращим був зразок із заміною 5 % ячмінного солоду. При цьому вміст редукуючих речовин становив 86,9 г

на 100 г екстракту, а вміст амінного азоту – 154,9 мг на 100 г екстракту. Отримане пиво має кращий результат за вмістом спирту (2,9 % масових) і за масовою часткою дійсного екстракту (5,53 % масових).

Зі збільшенням кількості обрушеної гречки та гречаного солоду кількість редукуючих речовин і амінного азоту зменшується, оскільки у ячмінному солоді недостатня кількість гідролітичних ферментів, під дією яких утворюються вищевказані речовини. Так, у зразку із заміною 5% ячмінного солоду на гречаний вміст редукуючих речовин становив 92 г на 100 г екстракту, а вміст амінного азоту – 168 мг на 100 г екстракту. У зразку із заміною 15% ячмінного солоду ці показники становлять 82 г на 100 г екстракту та 91 г на 100 г екстракту відповідно.

Висновки. Найкращою культурою для виробництва низькоглютенового пива є обрушена біла гречка та гречаний солод у співвідношенні 95:5.

Ключові слова: *глютен, гречка, ячмінь, солод, сусло, пиво.*

Вплив фізико-хімічних показників води на амінокислотний склад хлібного квасу

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Вступ. Визначено вплив підготовленої за допомогою клиноптилоліту, гірського кришталю та активного вугілля питної води на амінокислотний склад сусла і квасу.

Матеріали і методи. Підготовку води проводили шляхом її обробки клиноптилолітом, активним вугіллям і гірським кришталем. Зброджене сусло отримували ферментацією квасного сусла на житній основі дріжджами *Saccharomyces cerevisiae* МП-10. Амінокислотний склад сусла та квасу визначали методом іонообмінної хроматографії, динаміку бродіння квасного сусла – методом бродильної проби.

Результати і обговорення. В результаті оброблення води клиноптилолітом, активним вугіллям і гірським кришталем, загальна жорсткість знижувалася від 4,5 до 1,1 ммоль/дм^3, окислюваність перманганатна – від 4,0 до 0,5 мг O_2/дм^3, залізо і залишковий хлор видалялись повністю.

Зміна мінерального складу води суттєво впливала на перебіг технологічного процесу, кількісний і якісний амінокислотний склад сусла та квасу. Використання підготовленої води покращувало якісний склад амінокислот, збільшувало їх загальний вміст у початковому суслі від 3,3 до 8,87 мг/100 г, зокрема незамінних від 0,44 до 3,31 мг/100 г, що зменшувало їхнє ресинтезування, пере- та дезамінування дріжджовою клітиною. Загальна кількість амінокислот у зброженому суслі з використанням підготовленої води становила 9,88 мг/100 г, в контрольному – 5,57 мг/100 г.

Співвідношення амінокислот у суслі мало суттєві відмінності, зокрема вміст проліну, який важко засвоюється дріжджовою клітиною, при використанні підготовленої води становив 14%, а для контрольного зразка – 30%.

Інтенсифікація процесу культивування дріжджових клітин на 24 год збільшує їхню концентрацію в культуральній рідині від 96,8 до 85,1 млн/см^3, а також скорочує тривалість бродіння квасного сусла від 15 до 13 годин.

Амінокислотний скор квасу, приготовленого з використанням підготовленої води на стадіях культивування дріжджів і зброджування квасного сусла, був більш прийнятним порівняно із непідготовленою водою.

Висновки. Використання води, підготовленої за допомогою клиноптилоліту, гірського кришталю та активного вугілля, покращує якісний склад амінокислот і збільшує їх загальний вміст в початковому та зброженому суслі.

Ключові слова: *квас, бродіння, дріжджі, клиноптилоліт, активне вугілля, гірський кришталь, амінокислота.*

Вплив додавання борошна чуфи на характеристики йогурту

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Вступ. Мета дослідження – визначити вплив додавання борошна чуфи на характеристики йогурту.

Матеріали і методи. Йогурт готували, дотримуючись класичного технологічного процесу, з тією різницею, що в різних пропорціях додавали борошно чуфи (*Cyperus esculentus*) (зразок ІСО3–0,3%, ІСО5–0,5%, ІСО7–0,7%). Зразки йогурту витримували за температури 2–4 °С протягом 15 днів. Діацетил визначали методом газової хроматографії, титровану кислотність зразків йогурту - титруванням 0,1N NaOH, а синерезис – за методом Баркаллах.

Результати і обговорення. Після першого дня зберігання вміст діацетилу був низьким у всіх аналізованих зразках, але зразок ІСО5 продемонстрував більш високий вміст діацетилу – 6,5 мкг/г. Через 15 днів зберігання вміст діацетилу збільшився у всіх аналізованих зразках, тому вміст діацетилу в контрольному зразку становить 6,4 мкг/г, ІСО3 - 15 мкг/г, ІСО5 - 16,2 мкг/г та ІСО7 18,8 мг/г. Високий вміст діацетилу міститься в ІСО7, отже, додавання борошна чуфи має позитивний вплив на молочнокислі бактерії, що використовуються в процесі бродіння. Кислотність підвищувалася у всіх зразках йогурту, проаналізованих з 1-го по 15-й день. Контрольний зразок демонструє нижчі показники кислотності – від 80 до 108 °Т порівняно з іншими зразками, але зразок із борошном чуфи в пропорції 0,7% має значення кислотності між 87 і 125 °Т. Протягом 1-го та 15-го дня найвище виділення сироватки спостерігалось для контрольного зразка порівняно із зразками ІСО3, ІСО5 та ІСО7. Зразок ІСО7 демонструє нижчий синерезис: 1-й день – 9%, 15-й день – 32%.

Висновки. Додавання борошна чуфи покращує якість йогурту, що має особливе значення для споживача.

Ключові слова: *йогурт, чуфа, діацетил, якість.*

Вплив спіруліни та ламінарії на антиоксидантну активність пшеничного хліба

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Вступ. Вивчено вплив їстівних водоростей *Spirulina platensis* і *Kelp* на антиоксидантну активність пшеничного хліба.

Матеріали і методи. Хліб виготовлено з пшеничного борошна з додаванням порошку спіруліни (*Spirulina platensis)* та ламінарії (*Kelp*) у кількості 2 і 4% від маси борошна. Антиоксидантну активність етанольних екстрактів оцінювали трьома методами: FRAP (заліза, що зменшує антиоксидантну силу), методом очищення радикалів DPPH (2,2-дифеніл-1-пікрилгідразил) і аналізом вилучення гідроксильних радикалів (OH) (HRSA).

Результати і обговорення. Виявлено суттєві відмінності у вмісті загального поліфенолу серед різних кількостей водоростей і спіруліни, доданих у хліб. Найбільший вміст поліфенолів мав зразок хліба, що містить 4% спіруліни: 0,88±0,02 мг GAE/г сухих речовин, а найменший – зразок з 2% ламінарії: 0,44±0,05 мг GAE/г сухих речовин. Існує кореляція між вилученням радикалів DPPH і вмістом загального поліфенолу та флавоноїдів. Найвищу активність вилучення радикалів DPPH спостерігали у хлібі з добавкою 4% спіруліни – 3,11±0,05 ммоль TE/г сухих речовин. На відміну від цього, найнижча здатність до очищення DPPH спостерігалась у екстрактах етанолу з хліба з 4% ламінарії (0,89±0,02 ммоль TE/г сухих речовин). Антиоксидантна здатність етанолових екстрактів до зниження Fe_3+ за значеннями FRAP, що відображають коливаються від 2,77 (для зразка з 4% ламінарією) до 5,04 мкмоль Fe2+/г сухих речовин (для зразка з 4% спіруліни). При підвищеній концентрації спіруліни були помічені значні зміни в активності знешкодження гідроксильних радикалів. Найвищі значення становили 27,8±0,4 мкг BHT/г сухих речовин у зразку, приготовленому з 4% *Spirulina platensis*, та 17,16 ± 0,42 мкг BHT/г сухих речовин у хлібі, що містить 2% тих самих водоростей. Результат для контрольної проби становив 13,85±0,37 мкг BHT/г сухих речовин – вище значення, ніж для зразка з 2% (11,85 ± 0,42 мкг BHT/г сухих речовин) і 4% ламінарії (7,94±0,34 мкг BHT/г сухих речовин), як і при інших двох методах визначення антиоксидантної активності.

Висновки. Етанолові екстракти хліба, приготовані з додаванням 4% *Spirulina platensis*, мали найвищий вміст фенольних сполук і антиоксидантну активність, виміряну з використанням усіх методів.

Ключові слова: *хліб, спіруліна, ламінарія, антиоксидант.*

Реологічні властивості ягідних соусів з йодовмісних добавками

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Вступ. Мета дослідження – встановити вплив додавання водоростевої сировини та відсутності структуроутворювачів на реологічні характеристики ягідних соусів.

Матеріали і методи. Матеріалами реологічних досліджень були зразки чорнично-журавлинного соусу із соком калини з різним вмістом гідратованих водоростей і контрольні зразки з модифікованим кукурудзяним крохмалем та ксантановою камеддю. Дослідження реологічних властивостей проводили з використанням ротаційного віскозиметра. Органолептичні дослідження соусів проводили за п'ятибальною шкалою на основі вагового коефіцієнта.

Результати і обговорення. Криві залежності ефективної в'язкості від швидкості зсуву досліджуваних зразків подібні до кривих контрольних зразків у всіх серіях випробувань. Використання морських водоростей *Fucus* збільшує в'язкість соусів з дикорослих ягід без додаткових структуроутворювачів порівняно з контрольними зразками, виготовленими на основі ксантанової камеді, що обумовлене більшим значенням коефіцієнта консистенції, пропорційного в'язкості, який дорівнює для зразків з *Fucus* – 7,32 Па·с, з ксантановою камеддю – 7,22 Па·с. Використання водоростей замість ксантанової камеді та крохмалю покращує здатність макроскопічних систем самостійно відновлювати структуру після її руйнування, що доведено порівняно більшими значеннями коефіцієнтів тиксотропії. Так, коефіцієнт тиксотропії для зразків з ксантановою камеддю становить – 56,9%, з крохмалем – 64,0%, з *Laminaria* – 78,0%, з *Undaria pinnatifida* – 82,0%. Використання морських водоростей покращує структурні властивості пастеризованих об'єктів дослідження, що підтверджено зменшенням значення коефіцієнта консистенції, пропорційного в'язкості для зразків соусів порівняно з непастеризованими зразками – для зразків з *Undaria pinnatifida* – на 0,84 Па·с, з *Laminaria* – на 0,20 Па·с. Додавання до складу гідратованих водоростей (до 8% *Laminaria* та 3% *Fucus* та *Undaria pinnatifida*) не чинить негативного впливу на органолептичні та реологічні показники.

Висновки. Обґрунтовано виробництво ягідних соусів без додаткового додавання структуроутворювачів до рецептури.

Ключові слова: *ягоди, водорості, соус, йод, реологія, загущувач.*

Ефективність газохроматографічного аналізу терпенів і терпеноїдів як джерел ароматичних речовин з урахуванням полярності нерухомої фази

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Вступ. Метою дослідження є збільшення ефективності газохроматографічного аналізу терпенів та терпеноїдів на основі врахування полярності нерухомої фази.

Матеріали і методи. В дослідженнях використано модельну матрицю № 1 із суміші терпенів та модельну матрицю № 2 із суміші терпеноїдів. Матриці отримані препаративним виділенням в індивідуальному складі з підтвердженням чистоти виділення за індексом Ковача (ІК). Аналіз проводили на хроматографі GC 8000 series, газ-носій – гелій, детектор – полум`яно-іонізаційний (ПІД). Використано критерії вибору НФ GC аналізу за системою полярності Роршнайдера.

Результати і обговорення. При розділенні терпеноїдів (полярних АР) на неполярних НФ зв`язки, притаманні полярним молекулам (дипольні або водневі зв'язки) практично не виникають, тому терпеноїди утримуються на неполярній НФ SE-

30 значно слабше, ніж на полярній НФ Carbowax20M. Показовою є величина R_s. Чим вищі значення R_s, тим ефективніше працює газохроматографічна система розділення терпеноїдів. Для колонки з НФ Carbowax 20M R_s = 1,67, для колонки з НФ SE-30 R_s = 1,16.

Кількісною характеристикою універсальності досліджуваних НФ щодо поділу терпеноїдів за полярністю є різниця індексів Ковача ΔІК. Так, для ліналоолу на НФ SE-30 ІК = 1093, для Carbowax20M ІК = 1582. Це означає, що менш полярні терпеноїди будуть раніше покидати газохроматографічну колонку за більш полярні АР, забезпечуючи при цьому повне розділення складної суміші та можливість імовірного та відтворюваного встановлення компонентного складу дослідного зразка.

Час утримування терпенів зростає зі зменшенням полярності НФ. З двох дослідних НФ неполярна НФ SE-30 має більшу спорідненість з терпенами модельної матриці № 1, що виключає отримання на хроматограмах нерозділених піків для критичної пари компонентів з близькими $T_{кип}$.

Розраховані значення P_p за системою полярності Роршнайдера свідчать про різну полярність досліджуваних НФ і прояв характерних міжмолекулярних сил. При розділенні критичних пар терпенових вуглеводнів із близькими $T_{кип}$ (α-терпінен 172,5 ºС, d-лимонен 173 ºС, α-фелландрен 172 ºС) на неполярній нерухомій фазі (SE-30, P_p=4,40) спостерігається вихід компонентів з колонки нерозділеним піком. Застосування малополярної нерухомої фази (HP-5ms, P_p>15) забезпечує послідовний вихід критичних пар терпенових вуглеводнів окремими піками за $T_{кип}$.

Висновок. Результати досліджень дають змогу підвищити відтворюваність газохроматографічного аналізу джерел ароматичних речовин, а також вибирати НФ, які можуть бути взаємозамінними та забезпечувати аналогічне розділення, що зменшить витрати бюджету лабораторії.

Ключові слова: *хроматографія, терпени, терпеноїди, полярність, аромат.*

Процеси і обладнання

Удосконалення процесів функціонування систем електротехнологічної водоочистки за критерієм енергоефективності

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Вступ. Дослідження проводиться з метою обґрунтування та створення наукових основ функціонування електротехнологічних систем очистки стічних вод неперервних виробництв, функціонування яких відповідатиме вимогам ефективного використання енергетичних ресурсів та екологічної безпеки.

Матеріали і методи. Дослідження базується на методах активного та пасивного експериментів на дослідних установках і промисловому обладнанні, методі перехресних впливів способів водоочищення, методі домінуючого динамічного забруднювача, концепції моделювання на основі нотацій універсальної мови

моделювання UML для ефективної обробки вимірювальної інформації. Аналізуються підходи дослідження технологічних регламентів систем очистки стічних вод об’єктів неперервних виробництв з урахуванням критеріїв енергоефективності.

Результати і обговорення. Обґрунтовано архітектуру системи управління з адаптивним коригуванням стратегій управління в режимі реального часу. Система надає можливість прийняття рішень в умовах дії збурень природного і техногенного походження з урахуванням критерію енергоефективності. В узагальнену систему входять: локальна система управління і підсистема прийняття рішень з блоком фільтрації вхідного сигналу (підсистема прийняття рішень містить блок адаптивного формування стратегій управління в режимі реального часу на основі самоорганізованих карт Кохонена). Реалізовано підходи до об'єктно-орієнтованого створення і впровадження технологічних регламентів комбінованих електротехнологічних систем водоочистки переробної промисловості. Це дає змогу поліпшити енергоефективність процесів обробки багатокомпонентних стоків для підприємства м'ясопереробки шляхом відхилення критерію енергоефективності від нуля ± 9,6 %, малої металургії ± 3,4 %. Отримав подальший розвиток метод синтезу об'єктно-орієнтованих технологічних регламентів для вдосконалення алгоритмів керування комбінованими електротехнологічний системами водоочищення неперервних виробництв на основі критерію енергоефективності, який базується на оцінці ефективності використання енергоресурсів, як інтегрального параметра видалення забруднювачів із стоків. Інтелектуальне енергоефективне управління видаленням забруднювачів із стоків реалізується шляхом синтезу програмного та інформаційного забезпечення управління комбінованими електротехнологічними системами водоочистки на основі об’єктно-орієнтованих технологічних регламентів функціонування.

Висновки. Удосконалений метод управління функціонуванням електротехнологічних систем очистки стічних вод неперервних виробництв забезпечує дотримання вимог ефективного використання енергетичних ресурсів та екологічної безпеки.

Ключові слова: *контроль, регламенти, енергія, ефективність*.

Економіка

Оцінка ефективності корпоративної соціальної відповідальності компанії

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Вступ. Проаналізовано існуючі методології оцінки ефективності корпоративної соціальної відповідальності (КСВ).

Матеріали і методи. Для сучасних досліджень рівня розвитку КСВ підприємства використовувались якісні та кількісні методи дослідження для підприємств харчової промисловості України. КСВ повинна оцінюватися за рівнями. Кожен із цих рівнів має власну систему кількісних та якісних показників і різні методи, які можуть бути використані.

Результати і обговорення. У статті пропонується вдосконалена методика визначення інтегрального індексу ефективності КСВ, що розраховується за допомогою системи якісних та кількісних показників оцінки КСВ, які, на відміну від існуючих, враховують показники внутрішньої та зовнішньої КСВ.

Кількісні параметри внутрішньої КСВ включають такі групи, як задоволення інтересів власників через рентабельність компанії (коефіцієнт зміни рентабельності активів), задоволення інтересів персоналу (коефіцієнт зміни середньомісячної заробітної плати працівників), соціальні інвестиції – спрямування коштів на реалізацію внутрішніх програм (коефіцієнт зміни витрат на внутрішні соціальні програми), розвиток персоналу (коефіцієнт зміни частини працівників, які закінчили курси перепідготовки або підвищення кваліфікації) тощо. Кількісні параметри зовнішньої КСВ включають такі групи, як соціальні інвестиції у зовнішнє середовище (коефіцієнт зміни витрат на зовнішні соціальні програми), соціальні інвестиції на екологічні програми (коефіцієнт зміни витрат на екологічні програми). Значення коефіцієнта якісних параметрів розраховується відповідно до рівня розвитку КСВ підприємства на момент дослідження.

Висновки. Запропонована методика визначення інтегрального індексу дає змогу визначити рівень розвитку КСВ підприємства та розробити систему заходів щодо розвитку соціальної діяльності компанії.

Ключові слова: *відповідальність, КСВ, розвиток.*

Галузеві особливості формування конкурентоспроможності підприємств харчової промисловості: приклад України

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Вступ. Мета дослідження – визначення основних чинників, які обґрунтовують конкурентоспроможність українських підприємств різних галузей харчової промисловості на мезорівні, та оцінювання їхнього впливу на формування конкурентних переваг і недоліків.

Матеріали і методи. У ході дослідження використано контекстний порівняльний аналіз для виявлення факторів, що формують конкурентоспроможність українських підприємств різних галузей харчової промисловості. Для визначення сили впливу окремих чинників застосовувався метод експертного опитування.

Результати і обговорення. Основними факторами, які негативно впливають на конкурентоспроможність українських підприємств різних галузей харчової промисловості та викликають формування конкурентних недоліків (конкурентні слабкості, вади), є: олігополізація ринку, високий рівень тіньового сектора, зростання рівня конкуренції з компаніями і товарами, відсталий технічний рівень, застосування застарілих технологій, нестача сировини, залежність від імпортної сировини, технологій та устаткування, недостатньо відпрацьовані міжгалузеві взаємини, нерозвиненість системи логістичної інфраструктури сировини вітчизняного виробництва, недоступність до дешевих кредитних ресурсів, зниження купівельної спроможності населення.

До найбільш вагомих чинників, що позитивно впливають на стан підприємств галузей харчової промисловості та обґрунтовують формування конкурентних переваг

(конкурентної сили), віднесено: належність підприємств галузі до ТНК та/або інтегрованих структур, активність інноваційної діяльності та модернізація виробництва, відповідність продукції міжнародним стандартам, глибока переробка сировини, утилізація вторинної сировини і відходів, виробництво екологічної продукції, екологічність виробництва, сприятлива кон'юнктура ринків і темп їхнього зростання, наявність культури споживання.

Шляхи набуття та розвитку конкурентних переваг: адаптація підприємств до змін зовнішнього середовища, формування та розвиток інтегрованих об'єднань, оптимізація організаційної структури, раціоналізації управлінських і виробничих процесів з урахуванням галузевої специфіки та особливостей ведення бізнесу, запровадження екологічного виробництва.

Висновок. Проведений макроекономічний аналіз, що ґрунтується на авторській методиці, дає змогу визначити основні фактори, оцінити їхню силу впливу на конкурентоспроможність українських підприємств різних галузей харчової промисловості і запропонувати шляхи набуття та розвитку конкурентних переваг.

Ключові слова: *харчова промисловість, конкуренція, підприємство.*

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1. The title of the article
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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 – 2–3 lines, Materials and methods – 3-5 lines, Results and discussion – a half of page, Conclusion – 2 lines).
5. Keywords.
6. The main body of the article should contain the following parts:
   - Introduction
   - Materials and methods
   - Results and discussion
   - Conclusion
   - References

   If you need you can add another parts and/or divide them into subparts.
7. The information about the author (Name, surname, scientific degree, place of work, email and contact phone number).

All figures should be made in graphic editor, the font size 14.

The background of the graphs and charts should be only in white color. The color of the figure elements (lines, grid, text) – in black color.

Figures and EXCEL format files with graphs additionally should be submitted in separate files.

Photos are not recommended to be used as graphical materials.

Website of Ukrainian Food Journal: http://ufj.nuft.edu.ua

Email for all submissions and other inquiries: ufj_nuft@meta.ua

Шановні колеги!

Редакційна колегія наукового періодичного видання «**Ukrainian Food Journal**» запрошує Вас до публікації результатів наукових досліджень.

Вимоги до оформлення статей

Мова статей – англійська.

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

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

Всі поля сторінки – по 2 см.

Структура статті:

1**.** УДК**.**
2. **Назва статті.**
3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озерянко).
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
   - Матеріали та методи
   - Результати та обговорення
   - Висновки
   - Література.

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 2010 року.

Правила оформлення списку літератури

В Ukrainian Food Journalвзято за основу загальноприйняте в світі спрощене оформлення списку літератури згідно стандарту Garvard. Всі елементи посилання розділяються **лише комами**.

1. Посилання на статтю:

Автори А.А. (рік видання), Назва статті, Назва журналу (курсивом), Том (номер), сторінки.

Ініціали пишуться після прізвища.

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).

Зручні сайти для транслітерації:

З української мови – http://translit.kh.ua/#lat/passport

З російської мови – http://ru.translit.net/?account=mvd

Додаткова інформація та приклад оформлення статті – на сайті

http://ufj.ho.ua

Стаття надсилається за електронною адресою: ufj_nuft@meta.ua

УДК 663/664

Ukrainian Food Journal публікує оригінальні наукові статті, короткі повідомлення, оглядові статті, новини та огляди літератури.

Тематика публікацій в Ukrainian Food Journal:

Харчова інженерія
Харчова хімія
Мікробіологія
Фізичні властивості харчових продуктів
Якість та безпека харчових продуктів
Процеси та обладнання
Нанотехнології
Економіка та управління
Автоматизація процесів
Упаковка для харчових продуктів

Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

Ukrainian Food Journal індексується наукометричними базами:
Index Copernicus (2012)
EBSCO (2013)
Google Scholar (2013)
UlrichsWeb (2013)
Global Impact Factor (2014)
Online Library of University of Southern Denmark (2014)
CABI full text (2014)
Directory of Research Journals Indexing (DRJI) (2014)
Universal Impact Factor (2014)
Directory of Open Access scholarly Resources (ROAD) (2014)
European Reference Index for the Humanities and the Social Sciences (ERIH PLUS) (2014)
Directory of Open Access Journals (DOAJ) (2015)
InfoBase Index (2015)
Chemical Abstracts Service Source Index (CASSI) (2016)
Emerging Sourses Citaton Index (2018)

Рецензія рукопису статті. Матеріали, представлені для публікування в «Ukrainian Food Journal», проходять «Подвійне сліпе рецензування» двома вченими, призначеними редакційною колегією: один є членом редколегії і один незалежний учений.

Авторське право. Автори статей гарантують, що робота не є порушенням будь-яких авторських прав, та відшкодовують видавцю порушення даної гарантії. Опубліковані матеріали є правовою власністю видавця «**Ukrainian Food Journal**», якщо не узгоджено інше.

Політика академічної етики. Редакція «Ukrainian Food Journal» користується правилами академічної етики, викладених в роботі Miguel Roig (2003, 2006) "Avoiding plagiarism, self-plagiarism, and other questionable writing practices. A guide to ethical writing". Редакція пропонує авторам статей і рецензентам прямо слідувати цьому керівництву, щоб уникнути помилок у науковій літературі.

Інструкції для авторів та інша корисна інформація розміщені на сайті
http://ufj.ho.ua

Редакційна колегія

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