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Contents

Effect of the addition of *pinhão* flour and bagasse generated after starch extraction on the formulation of cookie

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Abstract

Introduction. After the process of the starch extraction from *pinhão* seeds, the generated residues are discarded. The aim of this study was to add these by-products as a potential substitute for wheat flour in a cookie formulation.

Materials and methods. *Pinhão* seed were purchased from local businesses in Ponta Grossa-PR (Brazil), and after the aqueous extraction of starch, the residues retained in the sieve were milled to produce a flour. The cookies were elaborated from a simplex-centroid experimental planning using wheat flour, whole *pinhão* flour and residual flour after the extraction of the *pinhão*.

Results and discussion. The flours produced with both *pinhão* and the bagasse obtained after the extraction of starch had high fibre content, and consequently, this was also seen in the cookies produced with the addition of these flours. Wheat flour had a higher protein (13.59±0.38%) and lipid (2.00±0.02%) content than *pinhão* and bagasse flours. Formulations using wheat flour and bagasse; or *pinhão* and bagasse had high lipid content (18.44±0.32% and 18.82± 0.09%, respectively). After cooking, the added bagasse biscuits showed a decrease in apparent and specific volume. The addition of *pinhão* flour to the biscuits provided greater softness, unlike the addition of bagasse. Differences were observed in the colour of the flours, especially in the luminosity and chromaticity a*. The wheat flour showed lower brightness possibly due to its higher ash content, impacting directly on the low brightness of biscuits produced with its addition. Besides making it difficult to grow the dough, the bagasse flour from starch extraction also made the cookies harder. The addition of the three flours, in equal proportion, showed interesting results for application in biscuits.

Conclusions. Both *pinhão* flour and bagasse obtained after starch extraction are potential sources of replacement for wheat flour, allowing adding value to this raw material considered endangered, as well as to the elaborated product.

Introduction

The trees of the so-called "Paraná pine" (*Araucaria angustifolia* or *Araucaria brasiliensis*, *Araucariaceae* family, order *Coniferales*) grow in mixed forests of southern Latin America: mainly in Brazil (south), Paraguay, Chile and Argentina. These trees can reach up to 35-60 m in height and up to 2 m in diameter and their wood has great value [1, 2]. The seeds of these trees are called *pinhão*. They have a high caloric value and can be consumed cooked or roasted by humans and domestic animals. Naturally they are eaten by birds and rodents [3].

In addition to proteins, lipids, fibres, complex carbohydrates, minerals and phenolic compounds, *pinhão* seeds contain about 68–72% starch [2, 4], which can be used in its native form or after modifications for industries such as pharmaceutical, food, cosmetic and textile [5, 6, 7, 9].

During the extraction of the amylaceous fraction, a fibrous by-product called bagasse is generated, which can still have a high content of starch and proteins [7]. This residue could be used in the formulation of some foods such as flour, in order to enrich the nutrition or replace wheat flour.

Thus, the objective of this study was to evaluate the effect of the addition of *pinhão* flour and bagasse generated after starch extraction on the formulation of cookies using the centroid-simplex design for experiments. Proximal analysis, colorimetry (L, a* and b*), analysis of physical properties and hardness were performed to characterise the biscuits.

Objectives of research:

- Produce a *pinhão* seed flour;
- Extract the starch and recover the bagasse;
- Formulate biscuits with whole wheat, *pinhão* flour and starch extraction bagasse;
- Analyse the proximal composition of biscuits;
- Determine the physical properties, colour and hardness of raw and baked cookie.

Materials and methods

Raw materials

Paraná pine seeds, whole wheat flour (F. Venturelli, F18), salt (L 317826), refined sugar, hydrogenated vegetable fat (Delicia Supreme, with salt, L 317826) and yeast (Royal, L.CC 32717 35 3) were acquired in the local commerce of Ponta Grossa (Paraná, Brazil).

Pinhão seeds were acquired in June (2018), and the skin and embryo were removed. The almonds were then kept at -18 °C in plastic bags for four months. After this period, the seeds were thawed (22 ºC).

Production of *pinhão* flour and aqueous starch extraction

For the production of *pinhão* flour, the seeds were initially submitted to aqueous grinding (1:1. m / v) in a mixer (Siemsen, model SL-08) and the product obtained was dried at 40 ºC for 18 h.

Starch extraction was performed by the aqueous method, starting with the aqueous grinding of the *pinhão* seeds as previously described, and passing the ground material through a sieve (150 mesh). The material retained in the mesh (bagasse) was resuspended in water and homogenized again with a blender to improve the extraction yield. After the second washing, the bagasse was recovered and dried in an oven at 40 ºC for 24 h, and the permeate was centrifuged to separate the starch.

After drying, the *pinhão* flour and the starch extraction bagasse were ground in a knife mill (Ika Werke M20 - 620 W) for 5 minutes and sieved (42 mesh) to homogenise the size of the particles.

Cookie formulation

The basic formulation of cookies is presented in Table 1.

Table 1

Basic formulation for standard integral cookies

Ingredients	Standard	% (m/m)[1]
Refined salt (g)	0.9	0.5
Yeast (g)	2.2	1.2
Refined sugar (g)	44.0	24.8
Hydrogenated vegetable fat (g)	30.0	16.9
Flour (g)	100.0	56.5
Distilled water (ml)	qsp[2]	-

[1]mass %;
[2]disregarding the volume of water;
[2]amount sufficient to reach the mass point

Centroide-simplex design for experiments was used to define the formulations, using 3 main components: (a) wheat flour, (b) *pinhão* nut flour, and (c) bagasse flour obtained after starch extraction (Figure 1).

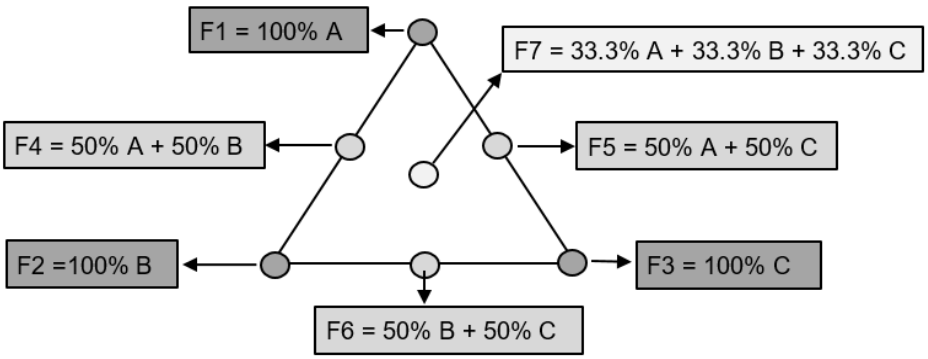

Fig. 1. Preview formulation after experimental planning:
F1 – wheat flour (A); F2 – *pinhão* flour (B); F3 – bagasse flour (C)

Thus, 7 assays were tested with different proportions of ingredients as shown in Table 2.

Table 2

Experimental planning for three compounds recipe

Formulation	Ratio of flour in ternary mixture					
	Pseudo-compounds			Real concentration (g)		
	A (X1)	B (X2)	C (X3)	A (C1)	B (C2)	C (C3)
1	1.00	0.00	0.0	100	0	0
2	0.00	1.00	0.00	0	100	0
3	0.00	0.00	1.00	0	0	100
4	0.50	0.50	0.00	50	50	0
5	0.50	0.00	0.50	50	0	50
6	0.00	0.50	0.50	0	50	50
7	0.33	0.33	0.33	33.3	33.3	33.3

(A) wheat flour, (B) *pinhão* flour and (C) bagasse flour obtained after starch extraction

All the ingredients were weighed, and the dough was mixed by hand. Water was added to obtain a uniform mixture. Then, the dough with a height of approximately 0.7 cm was cut with an aluminium baking sheet (4 x 4 cm) and kept in an industrial oven for 20 min at 180 ºC.

Centesimal composition

A centesimal composition of 3 flours and 7 formulations was performed. The protein content was performed by Kjeldahl and Soxlet [8].

The crude fibre content was performed by the sachet method (AOAC BA 6A-05). All determinations were performed in triplicate. The moisture and ash content were determined by thermogravimetry (TG) using the TGA-50 equipment (Shimadzu) under the following conditions: sample mass of approximately 7.0 mg; air atmosphere at a flow rate of 150 mL min^{-1}; heating ratio of 10 °C.min^{-1}, from 30 °C to 650 °C [3, 19]. The mass losses were calculated using the TA-60 software.

Physical properties

The length, width, thickness of the cookies were measured with a pachymeter. This analysis was performed on six randomly chosen biscuits before and after roasting. The ratio between the length and thickness of the biscuits after roasting results in the expansion factor. The mass of the raw and baked biscuits was determined with the aid of an analytical balance. The apparent volume (cm^3) of the baked biscuit was obtained by means of the method of displacement of birdseeds and the specific volume was calculated, dividing the apparent volume by the mass of the baked biscuit (cm^3 g^{-1}).

Colorimetric analysis

The MiniScan (Hunter) reflectance spectrophotometer was used to determine the colour parameters of the flours and raw and baked biscuits of the formulations. The equipment used was the portable colorimeter (Miniscan XE Plus, model 45/0-L, Hunter Associates Laboratory Inc., Reston, VA, USA) with CIE L*a*b* system [18]. Calibration was performed in accordance with the colour standards provided by the manufacturer. The biscuit was placed inside an opaque support in order to exclude the interference of external light in the sample. Colour measurements were initiated in six positions, totalling six colour readings of each biscuit.

Cookie hardness

The texturometer (TA.XT Plus Texture Analyser) and Texture Exponent Lite software was used to evaluate the hardness of the samples.

Seven days after baking, six biscuits were randomly selected and the experiment was performed in the 'Measure force in compression' mode (Ref BIS2/KB), under the following conditions: probe Knife Edge (HDP/BS) in base (HDP/90), velocities: pre-test of 1.5 mm s^{-1}; test of 2.0 mm s^{-1} and post-test of 10.0 mm s^{-1}, trigger force of 25g, distance of 5 mm, restarting in original position.

Statistical analysis

The results of the analyses were expressed as mean followed by standard deviation. Analysis of variance (ANOVA) and Tukey's test were used to compare the means between the samples with 95% confidence ($p < 0.05$).

Results and discussion

Centesimal composition

Flour is the product obtained from edible parts of one or more species of cereals, pulses, fruits, seeds, tubers and rhizomes by grinding and/or other technological processes considered safe for food production. The product is called "flour" followed by the name of the plant [10].

Pinhão flour can be produced from its edible parts, aiming at better utilization of its nutrients, adding value and as an alternative to the replacement of wheat flour, since it does not present gluten [11].

In the literature it is possible to find the production of *pinhão* flour from drying the endosperm at a temperature of 70 ºC for 4 h, in order to apply it to bread and biscuits [11, 12].

The centesimal composition of the wheat flour, *pinhão* and bagasse are presented in Table 3.

Pinhão flour (B) and flour obtained from starch extraction bagasse (C) can be classified as "rich" or with high fibre content in accordance with current national legislation [13], because they have a content greater than 6 g of fibre per 100 g of product. From the increase in fibre concentration, the flour (C) retained a greater amount of water, consequently, presenting higher moisture content.

Pinhão flour has higher carbohydrate content than wheat flour, while the amount of lipids, proteins and ashes is lower. The lipid content of flour (B) was similar to the values found in the literature [4, 14].

Table 3

Centesimal composition of (A) wheat flour, (B) *pinhão* flour and (C) bagasse flour obtained after starch extraction (% m/m)

Sample	Moisture	Carbohydrate[1]	Protein	Lipid	Total fibre	Ash
A	8.00±0.11^{b}	67.71±0.33^{c}	13.59±0.38^{a}	2.00±0.02^{a}	4.74±0.01^{b}	8.70±0.11^{a}
B	6.32±0.12^{c}	82.05±0.16^{a}	6.04±0.27^{b}	1.33±0.09^{b}	6.35±0.54^{ab}	4.27±0.16^{c}
C	8.64±0.03^{a}	79.87±0.03^{b}	4.53±0.03^{c}	1.47±0.04^{b}	8.49±0.06^{a}	5.50±0.02^{b}
p-value	<0.001	<0.001	<0.001	0.002747	0.029319	<0.001

^{abc}Different letters in the same column represent signific ant differences according to Tukey's Test ($p<0.05$).

The extraction of *pinhão* starch confers a reduction in the protein content and higher concentration of lipids, ashes and fibres in the bagasse.

These differences between the flours influenced the centesimal composition of the elaborated cookies, as shown in Table 4.

Table 4

Centesimal biscuit composition (% m/m)

Sample	Moisture	Carbohydrate[1]	Protein	Lipid	Total fibre	Ash
1	8.00±0.11^{a}	59.70±0.38^{e}	8.38±0.30^{a}	15.23±0.00^{bc}	5.95±0.86^{ab}	8.70±0.11^{b}
2	5.74±0.05^{c}	68.58±0.69^{b}	3.65±0.13^{d}	14.88±0.77^{c}	7.26±1.78^{ab}	7.15±0.12^{c}
3	6,39±0.06^{b}	72.25±0.27^{a}	3.05±0.24^{e}	14.95±0.04^{c}	8.04±0.61^{a}	3.36±0.03^{f}
4	6.33±0,06^{b}	67.99±0.25^{b}	5.77±0.15^{b}	15.36±0.21^{bc}	5.36±0.36^{ab}	4.55±0.05^{e}
5	4.33±0.23^{d}	63.08±0.14^{d}	5.67±0.11^{b}	18.44±0.32^{a}	7.52±1.87^{a}	8.49±0.24^{b}
6	8.05±0.05^{a}	60.00±0.16^{e}	3.32±0.04^{de}	18.82±0.09^{a}	4.48±0.31^{b}	9.81±0.14^{a}
7	5.50±0.04^{c}	66.64±0.25^{c}	4.93±0.13^{c}	16.40±0.18^{b}	5.79±0.65^{ab}	6.53±0.05^{d}
p-value	<0.001	<0.001	<0.001	<0.001	0.01	<0.001

[1]Calculated by difference

^{abc}Different letters in the same column represent significant differences according to Tukey's Test ($p<0.05$).

According to the Brazilian legislation, biscuits are the products obtained by the mixture of flour(s) and/or starch(es) with other ingredients, submitted to kneading and cooking processes, fermented or not. They may have different coverage, filling, shape and texture [13]. The biscuits made with bagasse had a higher content of carbohydrates, differing significantly from the other formulations. The protein content was higher in the formulation made only with wheat flour. The combination of wheat flour and bagasse flour, as well as bagasse flour and *pinhão* flour provided the highest lipid content in the cookies.

Higher ash content was obtained with the combination of *pinhão* flour and bagasse. The lowest content was found for the formulation with bagasse only.

The assay with the use of the three flours in equal proportion gave an interesting result for proximal composition, with a good content of fibres, proteins and lipids.

Physical properties

Regarding the evaluation of physical properties of the samples before and after cooking, the results are presented in Table 5.

Table 5

Evaluation of the physical properties of cookies before and after cooking

Raw cookie	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**p-value**
Length (cm)	3.8 ±0.1^{c}	3.8 ±0.1^{bc}	3.9 ±0.1a^{bc}	4.0 ±0.1^{ab}	3.9 ±0.1^{abc}	4.0 ±0.0^{a}	4.0 ±0.1^{ab}	<0.001
Width (cm)	3.8 ±0.1^{b}	3.9 ±0.1^{ab}	4.1 ±0.1^{a}	3.9 ±0.2^{ab}	3.9 ±0.1^{ab}	3.8 ±0.1^{b}	3.9 ±0.1^{b}	<0.001
Thickness (cm)	0.7 ±0.0^{b}	0.6 ±0.1^{c}	0.8 ±0.0^{a}	0.8 ±0.1^{ab}	0.8 ±0.0^{a}	0.8 ±0.1^{ab}	0.8 ±0.0^{a}	<0.001
Mass (g)	11.5 ±0.4^{b}	10.7 ±0.8^{b}	13.7 ±1.0^{a}	14.0 ±0.4^{a}	14.1 ±0.5^{a}	14.7 ±0.5^{a}	13.6 ±0.9^{a}	<0.001
Baked cookie	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**p-value**
Length (cm)	3.9 ±0.1^{c}	4.5 ±0.2^{a}	4.0 ±0.1^{bc}	4.4 ±0.2^{a}	4.0 ±0.1^{bc}	4.2 ±0.1^{b}	4.1 ±0.1^{bc}	<0.001
Width (cm)	4.0 ±0.1^{b}	4.4 ±0.1^{a}	4.0 ±0.1^{b}	4.5 ±0.1^{a}	4.1 ±0.1^{b}	4.1 ±0.2^{b}	4.1 ±0.1^{b}	<0.001
Thickness (cm)	1.0 ±0.1^{c}	1.1 ±0.1^{bc}	0.9 ±0.1^{c}	1.2 ±0.0^{a}	1.2 ±0.0^{a}	1.1 ±0.1^{bc}	1.2 ±0.1^{ab}	<0.001
Expansion factor	4.0 ±0.4^{ab}	4.3 ±0.5^{a}	4.3 ±0.2^{a}	3.6 ±0.1^{bc}	3.3 ±0.1^{c}	4.0 ±0.4^{ab}	3.6 ±0.4^{bc}	<0.001
Mass (g)	9.2 ±0.2^{c}	8.7 ±0.6^{c}	11.2 ±0.7^{b}	12.0 ±0.5^{ab}	11.6 ±0.3^{ab}	12.4 ±0.4^{a}	12.4 ±0.9^{a}	<0.001
Apparent volume (cm^3)	15.0 ±0.0^{b}	15.0 ±0.0^{b}	10.2 ±0.1^{c}	20.0 ±0.0^{a}	15.0 ±0.0^{b}	21.3 ±1.0^{a}	16.0 ±0.0^{b}	<0.001
Specific volume(cm^3 g^{-1})	1.6 ±0.0^{a}	1.7 ±0.1^{a}	0.9 ±0.1^{c}	1.7 ±0.1^{a}	1.3 ±0.0^{b}	1.7 ±0.0^{a}	1.3 ±0.1^{b}	0.44

^{abc}Different letters in the same line represent significant differences according to Tukey's Test ($p<0.05$).

The raw biscuits showed slight differences in their measurements during their modelling. Bagasse flour seems to interfere with the weighing of biscuits when compared to wheat and *pinhão* flours.

After baking the biscuits, a more significant increase was observed in the length, width and thickness of the biscuits for the formulation with *pinhão* flour. The balanced mixture between wheat and *pinhão* was influenced by the characteristics of *pinhão* flour, leaving it

lighter, and with width, length and thickness similar to formulation 2. So, *pinhão* flour made the dough lighter than wheat flour. Perez and Germani [15] also found lower weight for biscuits formulated with eggplant flour before and after roasting. Bagasse flour, which already had a higher dough in the raw cookie, seems to have resulted in a denser dough, hindering the growth of the dough, since its parameters were practically maintained after baking the biscuits.

The expansion factor is related to the quality of dough, evaluating the ability of the ingredients to absorb water, especially flour. Thus, biscuits formulated with higher fibre content are associated with higher water retention. With this, the expansion factor generally decreases. This was not observed in this study, as reported by other authors [16] with elaboration of cookies using pumpkin seed flour. These authors suggested that due to the high amount of insoluble fibres in pumpkin seeds this may not interfere with water absorption. Thus, the presence of fibres may favour a greater availability of water in the mass, allowing the gelatinisation of starch, and consequently, cause an increase in the expansion of the elaborate biscuits.

A reduction in apparent and specific volume was observed after the addition of bagasse. On the other hand, the mixture between wheat and *pinhão*, as well as *pinhão* and bagasse showed higher apparent volume.

As the biscuits with added bagasse flour showed higher mass after roasting, this affected their specific volume, being the lowest value found.

Colorimetric analysis

The results for the flours' colour parameters are presented in Table 6.

Table 6

Colour parameters of (A) wheat flour, (B) pinhão flour and (C) bagasse flour obtained after starch extraction

Flours	L	a*	b*
A	77.88±0.74^{c}	2.85±0.26^{a}	11.08±0.40^{a}
B	83.38±0.06^{b}	2.30±0.01^{b}	10.70±0.04^{a}
C	85.95±0.06^{a}	0.79±0.02^{c}	10.21±0.06^{b}
p-value	<0.001	<0.001	<0.001

^{abc}Different letters in the same column represent significant differences according to Tukey's Test ($p<0.05$).

Wheat flour showed higher ash content in the proximal analysis, and this reflected in lower luminosity. The chromaticity a* that evaluates the trend from green (-) to red (+) was lower for bagasse flour, thus a lower trend to red, unlike wheat flour. This may be related to the leaching of pigments during starch extraction. And for the chromaticity b* that evaluates the trend from green (-) to yellow (+), there was no significant difference between wheat flour and *pinhão* flour, with a greater tendency to yellow.

Tables 7 and 8 present the colour parameters for the raw and baked cookies, respectively.

Table 7

Colour parameters of raw cookies

Formulation	L	a*	b*
1	47.94±0.55^{g}	9.46±0.35^{a}	22.49±0.54^{a}
2	67.61±0.07^{a}	4.68±0.03^{e}	17.24±0.12^{e}
3	64.9±0.56^{b}	6.34±0.19^{d}	17.69±0.46^{de}
4	57.28±0.85^{e}	7.00±0.30^{c}	19.2±0.57^{c}
5	55.12±0.59^{f}	7.68±0.16^{b}	20.24±0.51^{b}
6	61.8±0.13^{c}	6.83±0.04^{c}	20.25±0.12^{b}
7	60.58±0.07^{d}	6.37±0.09^{d}	18.39±0.89^{cd}
p-value	<0.001	<0.001	<0.001

^{abc}Different letters in the same column represent significant differences according to Tukey's Test ($p<0.05$).

The colour of the cookies before being submitted to the oven, reflected the colour of the flours, with a higher luminosity, or tendency to white for *pinhão* flour and bagasse, and a higher tendency to red and yellow for wheat flour. Thus, the presence of wheat in the formulations decreased the luminosity of the samples and the chromaticity a* and b*.

Table 8

Colour parameters of baked cookies

Formulation	L	a*	b*
1	59.16±0,17^{f}	8.56±0.10^{a}	23.26±0.18^{c}
2	68.17±0,16^{c}	8.31±0.08^{b}	26.16±0.26^{a}
3	71.93±0,09^{a}	6.23±0.06^{f}	20.48±0.08^{e}
4	64.96±0,41^{e}	8.24±0.04^{b}	24.79±0.11^{b}
5	66.40±0,13^{d}	7.02±0.07^{c}	22.79±0.07^{c}
6	69.97±0,56^{b}	6.77±0.11^{d}	23.20±0.35^{c}
7	69.03±0,34^{c}	6.51±0.13^{e}	21.98±0.15^{d}
p-value	<0.001	<0.001	<0.001

^{abc}Different letters in the same column represent significant differences according to Tukey's Test ($p<0.05$).

Corroborating with the colorimetric analysis of the flours, after baking, the biscuits formulated with wheat presented darker and with greater tendency to red, approaching these results the biscuit with pinion flour, which presented greater tendency to yellow. This may be related to the occurrence of non-enzymatic reactions such as the caramelization reaction of sugar present in the mixture and also to the Maillard reaction, since the mixture presents a high amount of carbohydrates and a significant amount of proteins [17].

Cookie hardness

The hardness corresponds to the force over a maximum distance of a compression cycle and is plotted as the maximum peak height of this cycle during the test. The hardness values varied from 6.68 to 25.68 kg as shown in Table 9.

Table 9

Cookie hardness

Formulation	Hardness (kg)
1	18.80 ± 1.29^{b}
2	8.30 ± 0.97^{d}
3	25.68 ± 3.14^{a}
4	6.72 ± 1.15^{d}
5	7.03 ± 0.49^{d}
6	11.41 ± 1.39^{c}
7	6.68 ± 0.80^{d}
p-value	<0.001

[abc]Different letters in the same column represent significant differences according to Tukey's Test ($p<0.05$).

The greatest hardness was found for the formulation of biscuit produced only with the bagasse flour obtained after the starch extraction from *pinhão* seeds (3) possibly due to lower starch content, followed by the sample with whole wheat flour (1). The lowest values were observed for formulations with added *pinhão* flour.

The gluten protein network, present in wheat flour, is one of the factors responsible for the hardness of the biscuits. *Pinhão* does not present gluten in its composition, and the starch present in the flours, as well as its higher fibre content, collaborates in the absorption of water and consequent reduction of the hardness values.

Thus, the *pinhão* flour gave less hardness to the biscuits, bringing an interesting sensory characteristic to the formulation defined as the central point of the experimental design. This allows adding value to the by-product of starch extraction and taking advantage of the nutritional value of both wheat flour and *pinhão* flour.

Conclusions

Bagasse flour from the extraction of *pinhão* starch is a good alternative as a substitute for wheat flour, presenting a rich nutritional value, especially as a source of fibre. The production of flour allows extending the useful life of the *pinhão*, expanding its industrial applications and breaking the barrier of its seasonality.

In addition, the biscuit made with the mixture of the three flours stands out, with a good nutritional balance, colour and less hardness.

The bagasse flour together with the wheat flour also presented interesting values except for the higher lipid content of the biscuit.

Thus, the effect of replacing whole wheat flour by *pinhão* flour and by-product of starch extraction in the preparation of biscuits proved promising and other applications can be explored in future work.

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Conditions for the obtaining of tocopherols from deodorizing distillates of sunflower oil

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Abstract

Introduction. A deodorizer distillate is a byproduct of oil deodoration, a natural source of tocopherols. The methods of obtaining a native antioxidants from a sunflower deodorizer distillate was investigated in this study.

Materials and methods. The sunflower deodorizer distillates from a local enterprise were used in this work. The unsaponificated fraction of deodorizer distillate was separated by saponification. The kinetics of sunflower oil oxidation with/without antioxidants is investigated by the volumetric method.

Results and Discussion. Deodorizer distillate increased sunflower oil induction period of oxidation by 1.5 times. Antioxidant activity of obtained concentrates was proved by increase of the induction period of oil oxidation almost three times as result of them addition in the amount of 50 mg per 100 g. Thus, saponification of deodorizer distillate gives possibility to obtain sufficiently effective inhibitor of oxidation.

It was shown that more effective way of antioxidants concentrating from a deodorizer distillates was to dissolve it in n-hexane with further adsorption of tocopherols on the activated carbon. Tocopherols were proposed to be eluted from activated carbon by m-xylene, after evaporation of which a concentrate of tocopherols was obtained. Obtained concentrate increased in the period of sunflower oil oxidation induction by 4.2 times when 50 mg per 100 g of the antioxidant were added to the oil. The value of the rate constant of interaction of the peroxide radical with the inhibitor (K_7) for the obtained antioxidant was determined to be 10^6 mol/l·sec.

Conclusions. A method of obtaining tocopherol concentrates from sunflower oil deodorant was proposed. The efficacy of the obtained tocopherol concentrate as an antioxidant was proved.

Introduction

It is known, that α-tocopherol is one of the most active natural antioxidants. Tocopherols are registered as food additives: E306 (tocopherol mixture), E307 (α-tocopherol), E308 (γ-tocopherol) and E309 (δ-tocopherol) and are widely used both in food and in medicine (γ, δ-forms have high vitamin activity) [1]. The term "vitamin E" or tocopherol is used for a large group of natural substances that have similar biological activity. In addition to the most common in nature α -tocopherol, its 11 homologues and stereoisomers are known, all of them are currently isolated from vegetable oils or obtained synthetically [2]. Synthetic forms of tocopherols (labeled as "D, L" or "D") are approximately twice less active than natural [3]. Tokotrienols, which differ from tocopherols by the presence of unsaturated bonds in the carbohydrate chain, are also included to the "vitamin E" group. Subsequently, we will identify the total amount of tocopherols and tocotrienols as a tocopherol concentrate.

One of the main natural sources of tocopherols is vegetable oils. Their content in animal fats is very small and they are almost absent in fish fats. The amount of α-tocopherol, for example, in unrefined sunflower oil, is approximately from 45 to 75 mg per 100 g of oil, in soya oil – 75 – 170 mg per 100 g, in coconut oil – 3 – 8 mg per 100 g, etc. [4]. However, the amount of tocopherols is significantly reduced during process of refining oils, most of them are lost at the deodoration stage, where substances with specific smell and taste are distillated from oils at high temperatures and in deep vacuum. As a result, a by-product of deodorization (deodorizer distillate or deodistillate or scrubber oil) is formed, which contains predominantly fatty acids, triglycerides, mono-, diglycerides, sterols, tocopherols and others. shows The composition of deodorizer distillates from various vegetable oils are shown in Table 1 [5, 6, 7].

Table 1

Composition deodorizer distillates different oils (g/100 g)

Lipid fraction	Soy			Corn		Sunflower		Rape	
	1	2	3	4	5	6	7	8	9
Squalene	1,28	2,09	0,65	0,21	0,99	1	0,73	0,4	0,07
δ- tocopherol	4,41	5,59	2,01	0,12	0,12	-	-	0,18	0,31
β- tocopherol	0,52	0,36	0	0,06	0,08	-	-	0,18	0,14
γ- tocopherol	10,73	11,26	4,96	1,09	2,75	0,07	0,3	2,48	2,33
α- tocopherol	0,82	0,82	0,54	0,15	0,36	1,21	4,76	1,35	0,89
Campesterol	5,06	5,66	1,91	0,84	1,67	0,45	1,58	4,37	2,93
Stigmasterol	4,1	4,81	1,38	0,19	0,37	0,62	2,04	-	0,01
Phytosterol	7,9	8,34	3,03	1,68	3,38	2,6	8,60	6,24	4,05
Phytosteride	2,59	2,33	4,45	0,62	-	0,09	0,3	5,33	1,35
Monoglycerides	1,24	1,93	1,85	0,04	0,13	0	0,86	1,42	2,11
Diglycerides	2,7	3,79	8,06	0,54	1,26	0,66	1,89	3,85	3,87
Triglycerides	2,7	3,79	8,06	0,54	1,26	0,66	1,89	3,85	3,87
Fatty acids (on $C_{18:1}$)	33	32	73,8	81,2	77,1	70,82	39,2	39,2	42,8

The quantitative composition of palm oil deodorizer distillate was established in [5]: fatty acids 81,7%, acylglycerides – 14,4%, squalene – 0,8%, tocopherols – 0,5%, sterols – 0,4%, other substances – 2.2%. Typical composition of deodorizer distillate of olive oil

according to [8] was characterized by high content of squalene − 28%, free fatty acids – 33.4%, phytosterols – 4.6%. Sunflower oil deodorizer distillate contains high content of α-tocopherol.

It is also known that deodorizer distillates obtained during deodorization are characterized by higher content of tocopherols, sterols in comparison with a distillates obtained during distillation itself [10]. Thus, deodorizer distillates is a cheap source of valuable and useful substances such as tocopherols, sterols, squalene, and also fatty acids that have numerous industrial uses.

A number of basically different methods of tocopherol concentrate obtaining from deodorizer distillate are known. These methods include concentration of tocopherols by saponification of deodisystyllate, extraction of nonsaponificated substances, which contain also tocopherols [Pat. US20080015367, p. SU 1771474, p. EP0171009B1, p. RU 2485111 C1, p. US4550183 A, p. US4550183 A, p. US3335154A Pate. US2263550 A]. The disadvantage of this method is that besides tocopherols, all nonsaponificated substances are containing in deodistyllate concentrate reducing its value.

Another method of tocopherol concentration is the esterification of free fatty acids by lower monoatomic alcohols, followed by their extraction by polar and nonpolar solvents [Pat. US5660691 A, p. US5646311 A, p. US5487817 A, p. US4454329 A]. This methods is economically disadvantageous in comparison with other described methods, since the process of esterification is multistage and requires expensive equipment. Sometimes the combination of these two methods are using but still the esterification of free fatty acids is using [Pat. US7575767 B2].

Finally, the concentration of tocopherols by their adsorption on ion-exchange resins is using [Pat. US3122565 A]. This method is the most attractive, since it does not require multi-stage processing. However, selection of technological and economical best adsorbent is necessary for its most effective use.

Actually, deodorizer distillates are not used as a source of tocopherols. However, the capacity of domestic enterprises for the processing of sunflower oil is significant, and therefore the development of technology for obtaining the valuable products from a deodorizer distillates is a significant task.

The known methods for producing tocopherols from deodorizer distillates are multistage, require the high temperatures and deep vacuum, that is, expensive equipment and high energy consumption.

The objective of this work was to develop the simple and cheap method for obtaining of native antioxidant − tocopherol concentrate from sunflower deodorizer distillates including as few stages as possible, not requiring high temperatures and providing high antioxidant activity.

Materials and methods

Sunflower deodorizer distillates, activated carbon RAN-200 were used for tocopherols obtaining. Refining dedorizated winterizated sunflower oil was used as model substance for determination of tocopherol concentrates antioxidant activity.

Proximate analyses of oxidation

Content of initial oxidation products was estimated according to peroxide value. Content of aldehydes and ketones (secondary oxidation products) was investigated by the method of determination of carbonyl compounds.

Separation of nonsaponificated and saponificated substances of deodorizer distillates

Saponification of deodorizer distillate was carried out by heating it to 75 ºC and adding a water-alcohol 0.5 mol/dm^3 solution of potassium hydroxide. Saponification was performed during 1 hour at constant stirring. After this, the nonsaponificated substances were extracteded from the reaction mixture with n-hexane followed by distillation of the solvent. [11].

Recovering the tocopherols from deodorant distillates

The separation of tocopherols on activated carbon was carried out according to the following procedure: the deodorant distillate was dissolved in n-hexane in the ratio 1:1.5 – 1:5, respectively. The resulting solution was passed twice through a column filled with a layer of activated carbon. The tocopherols were eluated from carbon column by m-xylene and m-xylene was distilled from eluate at 139.1 °C and obtained residue was a tocopherol concentrate.

Determination of sunflower oil oxidation kinetics

The kinetics of sunflower oil oxidation was investigated by the volumetric method [12]. The mesuaring was carried out at 70 º C under conditions of initiated oxidation, that is, due to the thermal decomposition of the solution of AIBN (azoizobutyronitrile), concentration of AIBN was 2 Mmol for all samples, that provided the constant oxidation rate initiation. The value of the induction period (τ, c) was determined by graphical method. This value is equal to the segment of the abscissa, which is cut off by a perpendicular from the point of intersection of the tangents to the kinetic curve.

The fixed amount of antioxidants – 2 mg/100 g was added to the samples of oil. Antioxidant concentration ([InH], mol/L) was determined according to equation [12]:

$$[InH] = \frac{1 \times [AIBN] \times (1 - e^{-K_p \times \tau})}{f} = 0,48 \times [AIBN] \times (1 - 0,9999^{\tau}), \qquad (1)$$

where [AIBN] – initiator concentration, mol/L; K_p – constant of rate of initiator decomposition at 70 ^{0}C ($3,9 \cdot 10^{-5}$ sec^{-1}); 1/f = 0.48 (1- radical quantity under destruction of one initiator molecule), τ – determined induction period, sec.

Determination of the rate constant of the oxidation chains termination

The antioxidant activity of obtained tocopherol concentrate was estimated as a rate constant of the oxidation chains decay (K_7) [12]. The 0.3 g tocopherol concentrate obtained were dissolved in 50 ml of xylene, and 0.1ml of solution was added to 5ml of cumene (the concentration of tocopherols approximately equal to their concentration in refined sunflower oil). The rate of oxidation of this solution was determined under different concentration of the initiator of oxidation (from 10^{-3} to 10^{-2} mol / L).

The reaction rate constant was calculated according to:

$$K_p / K_7 = tg\alpha \times \Delta V / [RH] \times \nu, \qquad (2)$$

where tgα – tangent of the slope angle of line, which reflects the dependence of the oxidation rate on the rate of initiation of cumene enriched with tocopherols, ΔV - volume of 1mm^3 oxygen, under normal condition $\Delta V = 4,09 \times 10^{-5}$ Mol/L; [*RH*]– hydrocarbon concentration; ν – sample volume, l; K_p – rate constant of the cumene oxidation, at 70 °C K_p = *3,19* L/mol·sec [12].

Results and discussion

Influence of sunflower deodorizer distillate and its unsaponificated fraction on the induction period of sunflower oil oxidation

The sunflower deodorizer distillate and its unsaponificated fraction were tested as inhibitors of oxidation. The kinetics of oxidation of sunflower refined oil were analyzed with the addition of 0.05% deodorizer distillate or unsaponificated substances. The results are shown in the Table 2.

Table 2

Parameters of sunflower refined oil oxidation under addition of deodorizer distillate and unsaponificated substances

Sunflower refined oil sample	Induction period of oxidation, sec	Inhibitor concentration, mol/L
Sunflower refined oil	1320	$1,1 \times 10^{-4}$
Sunflower refined oil + deodorizer distillate	1980	$1,7 \times 10^{-4}$
Sunflower refined oil + unsaponificated substances	4200	$3,2 \times 10^{-4}$

Unsaponificated fraction of deodorizer distillate increases sunflower oil induction period by 2.9 times, while deodorizer distillate itself only by 1.5 times. Thus, saponification of deodorizer distillate gives possibility to obtain sufficiently effective inhibitor of oxidation. Also, when applying this approach, a by-product – soap, which is also a commodity product [13], is produced.

For further increase of tocopherol concentration and subtiantly the antioxidant activity of concentrate the method of tocopherols recovering using their absorption on activated carbon was investigated.

Effect of antioxidant, obtained using activated carbon, on the oxidation kinetics of sunflower oil

The concentrate of tocopherols, obtained after purification on the carbon column, when added 0,05 % to sunflower oil extended its induction period of oxidation from 1320 sec to 5600 sec (4.2 times, Figure 1). These data proved that proposed method of tocopherols recovering from unsaponificated fraction of deodorizer distillate is available for purification and concentration of tocopherols.

Antioxidant activity of the obtained tocopherol concentrate

For estimation of antioxidant activity of the obtained tocopherol concentrate the rate constant of interaction of peroxide radicals with the inhibitor (K_7) was measured. Cumene was chosen as oxidation medium, an effective reducing agent whose oxidation rates are well studied and known [12]. Oxidation kinetics of cumene in the presence of obtained tocopherol concentrate under different concentration of AIBN are shown in Figure 2.

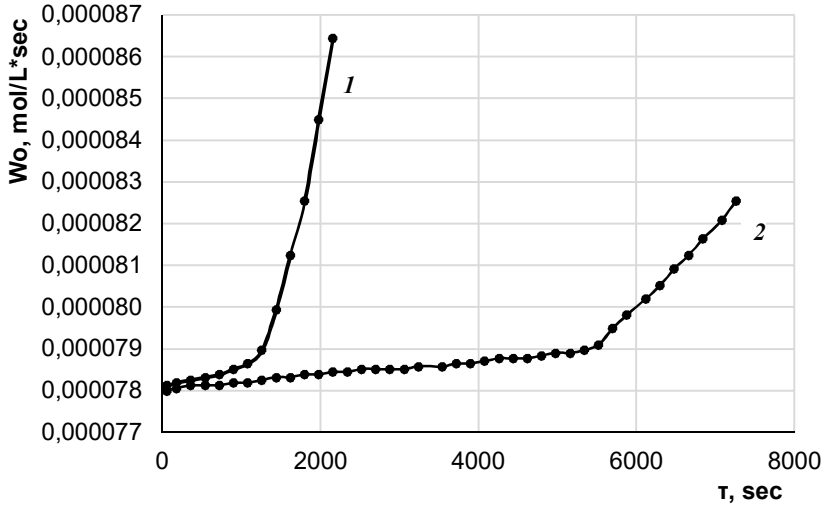

Figure 1. Oxidation kinetics of sunflower oil:
1 – sunflower refined oil, 2 – sunflower refined oil with addition of tocopherols concentrate, purified by carbon absorption

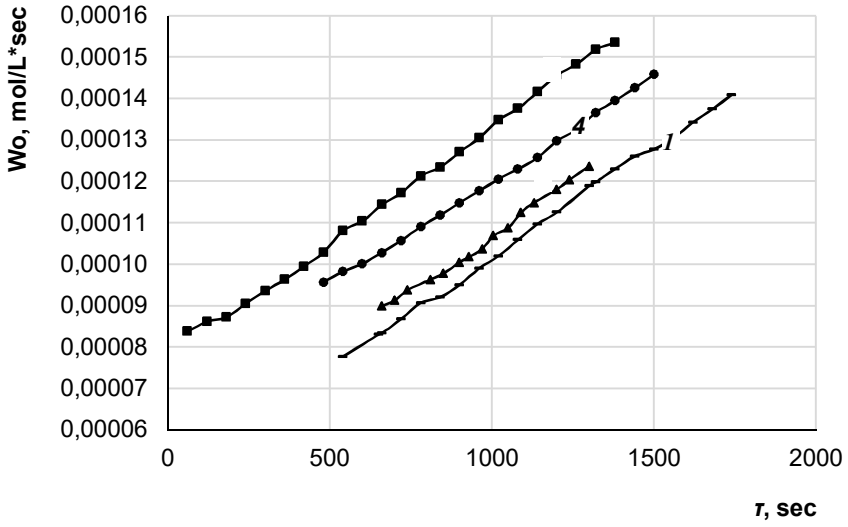

Figure 2. Kinetics of cumene oxidation in the presence of obtained antioxidant concentrate at different concentrations of AIBN:
1 – $4 \cdot 10^{-3}$ mol/L AIBN, 2 – $5 \cdot 10^{-3}$ mol/L, 3 – $6 \cdot 10^{-3}$ mol/L, 4 – $8 \cdot 10^{-3}$ mol/L

The rate constant of interaction of peroxide radicals with the inhibitor (K_7) was determined graphically as the value of a segment on the Y axis, cutted by the line of dependence between the rate of oxidation and the rate of initiation of cumene in the presence of antioxidant (Figure 3).

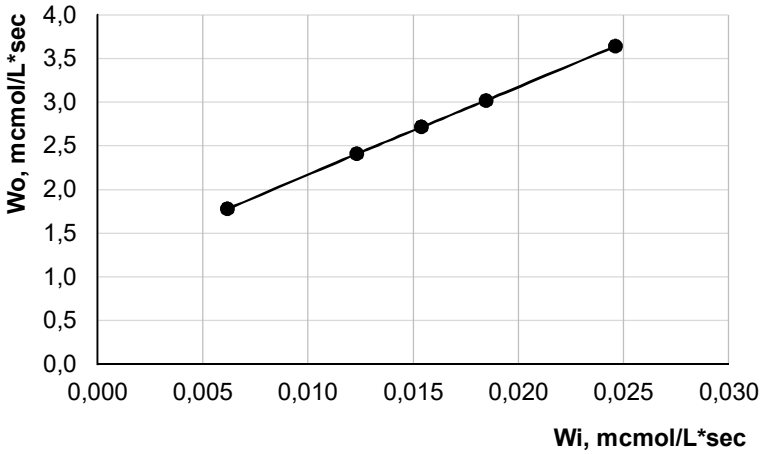

Figure 3. Dependence of the oxidation rate on the initiation rate of cumene in the presence of obtained antioxidant

The rate constant of the reaction between the inhibitor and the peroxide radical was also determined according to equation (2) and was $K_7 = 0.94 \cdot 10^6$ L/mol·sec. The obtained value approximately agreed with the known K_7 constants for tocopherols [12], that is, the obtained oxidation inhibitor can be recommended as a tocopherol concentrate.

Content of oxidation products in deodorizer distillate and isolated antioxidant

Content of oxidation products in different antioxidant fraction was determined in obtained concentrates (Table 3). Content of peroxides and carbonic substances was the lowest in tocopherols concentrate, obtained by absorption purification, and highest in the initial sunflower deodorizer distillate.

Thus developed method of tocopherols concentrate obtaining includes the next steps:

(A) the deodorizer distillate is dissolved in n-hexane in a ratio of 1:1.5 to 1:3 in order to reduce its viscosity and improve the contact of tocopherols with activated carbon (in another case it is enough to warm distillate up to 5 ºC of its melting point);

(B) the obtaining solution is passed through a layer of activated carbon, on which the tocopherols are absorbed, and most of other components are passed;

(C) to remove tocopherols from the adsorbent polar solvent m-xylene in the ratio m-xylene:deodorizer distillate from 1:1,5 to 1:3 is passed through the layer of activated carbon;

(D) m-xylene is evaporated from the tocopherols concentrate at 139.1 °C.

Table 3

Content of oxidation products in deodorizer distillate and isolated antioxidant

Sample	Peroxide value, mmol 1/2 O/kg	Carbonyl value, mg KOH/g
Sunflower deodorizer distillate	31,5	86,9
Unsaponificated substances of sunflower deodorizer distillate	15,5	56,1
Tocopherols concentrate, obtained by absorption purification	10,0	38,5

Using of the developed method for tocopherols concentrate obtaining gives the following advantages compared to the known technology: it does not require a multi-stage approach [14], which usually includes the distillation of deodorizer distillates and esterification of fatty acids and other components. It gives the opportunity to receive not only a tocopherol concentrate as a commercial product, but also a mixture of fatty acids and sterols, which can be used as a suitable raw material for the further removal of sterols and fatty acids. Adsorbent and solvents can be completely regenerated, that reduces the cost of the final product.

In addition the content, of benzpirene in the obtaining concentrate of tocopherols is significantly reduced compared to the content of benzpirene in the initial deodorizer distillate because of limited solubility of benzpirene in hexane. However, in case of the presence of this toxic substance in the final concentrate of tocopherols such samples can be recommended to be used for technical purposes. For example, in the production of lubricant and cooling products based on vegetable oils, antioxidants need to be used [15]. Lubricant and cooling products are traditionally obtained from the mineral oils. However, such materials are one of the main pollutants of the environment, and it is promising to replace them with vegetable oils [16].

The obtained concentrate of tocopherols also contains phytosterols, which are valuable biologically active substances. The tocopherols concentrate obtained from deodorizer distillate with a low content of benzpirene can be recommended for use in the food production.

Conclusions

1. Cost-effective method of obtaining a tocopherols concentrate from a by-product of oil refining – sunflower deodorizer distillate was developed. Efficiency as an antioxidant of the obtained concentrate is proved.

2. The scientific novelty of the work is to study the antioxidant effect of the obtained tocopherol concentrate. The reaction rate constant between the inhibitor and the peroxide radical was $K_7 = 0.94 \cdot 10^6$ L/mol·s, which proves the effectiveness of using the obtained tocopherol concentrate as an antioxidant.

3. The prospective methods of tocopherols extracting include the idea of saponification of deodorizer distillate at the first stage and the concentration of tocopherols on the activated carbon at the second stage. In this case most of the deodorizer distillate is separated at the first stage, that reduces the required amount of activated carbon and allows to obtain a product with a high content of tocopherols.

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Aromatic characterization and total volatile composition of red wines from the region of Central Northern Bulgaria

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Abstract

Introduction. The aromatic potential of the wine is based on the presence and variety (quantitative and species) of compounds of the groups of esters, higher alcohols, aldehydes, monoterpenes, methoxypyrazines, aliphatics, phenylpropanoids and others.

Materials and methods. The object of the present study were red wines obtained from Rubin, Storgozia, Bouquet, Trapezitsa, Kaylashki rubin and Pinot Noir grapevine varieties cultivated in the Experimental Base of the IVE. The alcohol content of the obtained wines was defined by specialized equipment with high precision – automatic distillation unit – DEE Destillation Unit with Densimat and Alcomat, Gibertini, Milan, Italy. Gas chromatographic determination of the aromatic components in wine distillates was done.

Results and discussion. Twenty eight volatile compounds have been identified. The greatest variety of volatile compounds (22 identified) in red wine of the Rubin variety was found. The lowest content (11 identified compounds) in the wine from Storgozia was established.

Considering the total content of volatile compounds, their lowest amount was found in the Trapezitsa wine (368.41 $mg.dm^{-3}$). The highest total volatile content was found in the Kaylashki rubin wine (1202.55 $mg.dm^{-3}$).

The total amount of higher alcohols was lowest (101.48 $mg.dm^{-3}$) in the Rubin wine. This quantity was significantly lower compared to the results for this indicator in all red wines examined. The highest content of higher alcohols (504.84 $mg.dm^{-3}$) was found in the Kaylashki rubin wine. A single aldehyde – acetaldehyde was identified in the wines studied. Very high total ester content (501.79 $mg.dm^{-3}$) was found in the Kaylashki rubin wine. Five terpene alcohols were found in the wines studied.

Conclusions. The present study proved that red wines obtained from hybrid Bulgarian varieties (obtained by intra- and iter-species hybridization) were characterized by a complex and varied volatile composition similar to that of *Vitis vinifera* L.

Introduction

The content of a variety of volatile compounds with a pronounced and heterogeneous aromatic effect is an indicator of wine quality. More than 800 volatile compounds with a total quantity ranging up to 800 mg.dm^{-3} and higher – 1200.00 mg.dm^{-3} [1, 2] have been identified in the wine. Factors influencing the synthesis and quantitative accumulation of the volatile components in grapes and wine are highly variable. They are mainly concentrated in: the genetic potential of the varieties to synthesize and accumulate volatile components with pronounced aromatic influence [3]; climate, soils, geographical location of the vine growing [4, 5]; agro-technical measures [6]; phytosanitary status of the vine [7,8]; the technical and technological conditions of vinification [9]; metabolic potential and activity of yeasts microflora (alcoholic fermentation) and bacterial lactic acid microflora (malolactic fermentation) [10, 11]; the wine aging processes [12, 13].

The aromatic potential of the wine is based on the presence and variety (quantitative and species) of compounds of the groups of esters, higher alcohols, aldehydes, monoterpenes, methoxypyrazines, aliphatics, phenylpropanoids and others [14, 15].

The esters have the most significant contribution to the aroma profile of the wine. Their low threshold of perception distinguishes them as the main and strong factor for the quality of the aroma. Their formation begins in the grapevine. Their amounts in grapes are varietal characteristic and low (10.00 – 30.00 mg.dm^{-3}) [16]. The biological ester synthesis from the yeasts results in significant accumulations (up to 500.00 mg.dm^{-3}) in young wines after vinification [11]. The wine aging process leads to a chemical bonding between the available alcohols and acids (esterification), which significantly increases the total ester content (792.00 – 880.00 mg.dm^{-3}) in old wines [17].

The esters having a major influence on the aroma and bouquet of wines include ethyl acetate, ethyl hexanoate, ethyl butyrate, isobutyl acetate, isoamyl acetate, hexyl acetate, ethyl decanoate, phenyl acetate, ethyl lactate [18, 19].

The higher alcohols also represent an important group of compounds from the volatile composition of the wine. They have high thresholds of aromatic perception, in contrast to the esters. This determines their weaker aromatic influence. However, their important contribution is related to their role as precursors in the esterification process, forming different esters with the wine acids [13]. The higher alcohols are mainly synthesized during alcoholic fermentation as a product of yeasts amino acid metabolism. Their concentration in red wines can reach up to 600.00 mg.dm^{-3} [11]. The major representatives of this group of compounds are 3-methyl-1-butanol (isoamyl alcohol), isobutyl alcohol, phenylethyl alcohol, hexanol, heptanol, butanol [19, 20, 13].

The aldehydes are quantitated mainly by acetaldehyde. The permissible concentration of this substance in dry wines ranges from 10.00 to 200.00 mg.dm^{-3} [11].

The terpenic profile of the wine is represented by the terpene alcohols linalool, α-terpineol, β-citronellol, nerol and geraniol [21, 22]. They have a fundamental contribution to the aroma of wines obtained from muscat grapevine varieties [23, 24].

The aim of the present study is to perform the aromatic characterization and identification of the total volatile composition of red wines from the region of Pleven, Central Northern Bulgaria.

Materials and methods

Grapevine varieties and vinification.

The study was conducted at the Institute of Viticulture and Enology (IVE) – Pleven, Central Northern Bulgaria. The object of the present study were red wines obtained from Rubin, Storgozia, Bouquet, Trapezitsa, Kaylashki rubin and Pinot Noir grapevine varieties cultivated in the Experimental Base of the IVE.

Pinot Noir is a widespread variety of *Vitis vinifera* L. It was used for control variant in the present study. The remaining varieties were hybrids selected in the IVE-Pleven, via the intra- and interspecies hybridization, whose parental forms were as follows:

- Rubin – Nebiolo x Shiraz [25];
- Storgozia – Bouquet x Villar Blanc [26];
- Bouquet – Mavrud x Pinot noir [25];
- Trapezitsa – Danube Gamza x Marseilles early [27];
- Danube Gamza – Bouquet x Villar Blanc [25];
- Kaylashky rubin – (Pamid x Hybrid VI 2/15) x (Gamma noir x *Vitis amurensis*) [27];

The grapes from the different varieties were harvested (30 kg for each variety) and were vinified at the Experimental Wine Cellar of IVE. A classic scheme for the production of dry red wines [28] was applied – crushing and destemming, sulphitation (50 mg/kg SO_2), inoculating with pure culture dry yeasts *Saccharomyces cerevisiae* Siha Rubio Cru (EATON Begerow) – 20 g/hl, temperature of fermentation – 28 °C, separation from solids, further sulphitation, storage.

Determination of alcohol content of obtained wines

The alcohol content of the obtained wines was defined by specialized equipment with high precision – automatic distillation unit – DEE Destillation Unit with Densimat and Alcomat, Gibertini, Milan, Italy.

Aromatic content determination by GC-FID

Gas chromatographic determination of the aromatic components in wine distillates was done. The content of major volatile aromatic compounds was determined on the basis of stock standard solution prepared in accordance with the IS method 3752:2005 [29]. The method describes the preparation of standard solution with one congener, but the step of preparation was followed for the preparation of a solution with more compounds. The standard solution in this study include the compounds with purity > 99.0%. The 2 µl of prepared standard solution was injected in gas chromatograph Varian 3900 (Varian Analytical Instruments, Walnut Creek, California, USA) with a capillary column VF max MS (30 m, 0.25 mm ID, DF = 0.25 µm), equipped with a flame ionization detector (FID). The used carrier gas was He. Hydrogen to support combustion was supplied to the chromatograph via a hydrogen bottle. The injection was manually by microsyringe.

The parameters of the gas chromatographic determination were: injector temperature – 220 °C; detector temperature – 250 °C, initial oven temperature – 35 °C/retention 1 min, rise to 55 °C with step of 2 °C/min for 11 min, rise to 230 °C with step of 15 °C/min for 3 min. Total time of chromatography analysis – 25.67 min. The identified retention times of the compounds in standard solution were: acetaldehyde (3.141), ethyl acetate (3.758), methanol

(3.871), 2-propanol (5.170), isopropyl acetate (5.975), 1–propanol (6.568), 2–butanol (7.731), propyl acetate (9.403), 2–methyl-propanol (10.970), 1–butanol (11.509), isobutyl acetate (11.662), ethyl butyrate (12.710), butyl acetate (12.752), 2–methyl-1-butanol (13.054), 4-methyl-2-pentanol (13.629), 3–methyl-1–butanol (13.840), 1–pentanol (15.180), isopenthyl acetate (15.965), pentyl acetate (16.033), 1–hexanol (16.276), ethyl hexanoate (16.376), hexyl acetate (16.510), 1–heptanol (16.596), linalool oxide (16.684), phenyl acetate (18.055), ethyl caprylate (18.625), α-terpineol (19.066), 2-phenyl ethanol (19.369), nerol (19.694), β-citronellol (19.743), geraniol (19.831), ethyl decanoate (19.904). As an internal standard 1-octanol was used. The resulting chromatographic profile of the standard solution is shown in Figure 1.

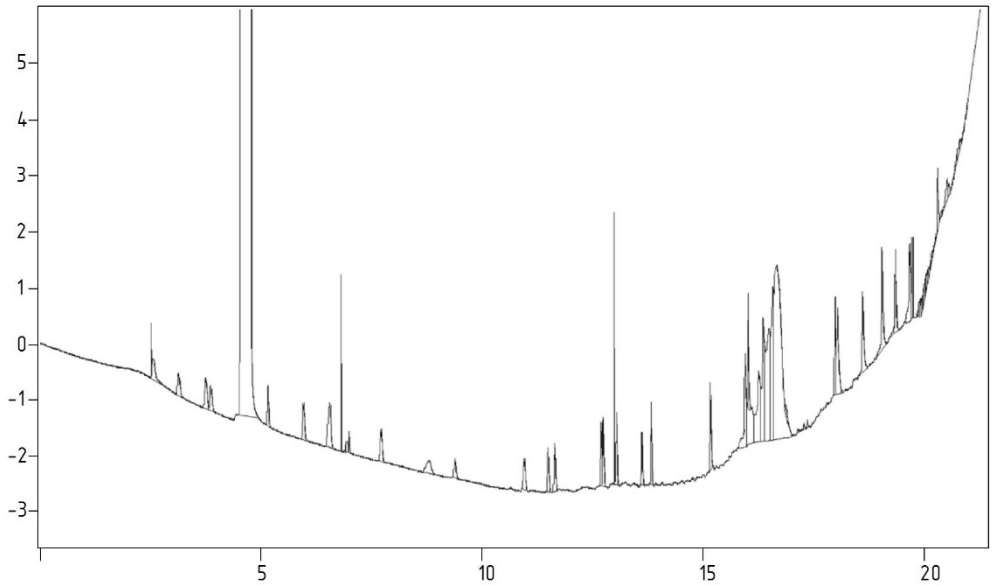

Figure 1. Chromatogram of standard solution

After determination of the retention times of aromatic compounds in the standard solution, we proceed to the identification and quantification of the volatile aromatic substances in the wines. The aromatic composition was determined based on injection of wine distillates. Prepared samples were injected in an amount of 2 µl in a gas chromatograph and was carried out an identification and quantification of the aromatic substances in each of them.

Results and discussion

The quantity of the identified compounds is presented in Table 1.

Table 1

Content of volatile aromatic compounds in red wines of Rubin, Storgozia, Bouquet, Trapezitsa, Kaylashki rubin and Pinot Noir

Identified compounds, $mg.dm^{-3}$	WINES					
	Rubin	**Storgozia**	**Bouquet**	**Trapezitsa**	**Kaylashki Rubin**	**Pinot Noir**
Ethyl alcohol, vol. %	12.72	11.39	13.53	14.75	12.65	14.91
Acetaldehyde	34.73	0.05	0.05	20.49	69.85	0.05
Methanol	22.02	75.75	36.63	40.91	126.07	50.59
1. Higher alcohols						
1-propanol	0.05	0.05	0.05	8.32	0.05	0.05
2-propanol	0.05	0.05	0.05	0.05	0.05	0.05
2-butanol	30.82	87.79	69.56	ND	62.00	44.71
2-methyl-1-buthanol	33.27	66.11	59.09	51.00	68.14	37.84
3- methyl -1-buthanol	37.19	273.63	220.74	181.39	241.42	199.12
4-methyl-2-pentanol	ND	ND	ND	ND	ND	0.05
1-pentanol	ND	ND	ND	ND	ND	31.45
1-hexanol	ND	ND	ND	ND	0.05	ND
1-heptanol	0.05	ND	ND	ND	ND	ND
2-phenyl ethanol	0.05	ND	ND	11.59	133.13	ND
Total higher alcohols	**101.48**	**427.63**	**349.49**	**252.35**	**504.84**	**313.27**
2. Esters						
Ethyl acetate	20.40	25.67	29.41	18.76	77.95	30.24
Propyl acetate	0.05	ND	ND	ND	ND	ND
Isobutyl acetate	ND	ND	ND	ND	273.23	ND
Ethyl butyrate	83.74	ND	ND	0.05	ND	ND
Ethyl hexanoate	ND	0.05	ND	ND	ND	ND
Pentyl acetate	ND	ND	ND	ND	0.05	0.05
Isopentyl acetate	156.85	ND	ND	ND	ND	ND
Hexyl acetate	ND	ND	ND	ND	0.05	ND
Phenyl acetate	0.05	ND	ND	ND	0.05	ND
Ethyl caprylate	0.05	0.05	ND	34.41	150.46	ND
Ethyl decanoate	0.05	ND	153.71	ND	ND	ND
Total esters	**261.19**	**25.72**	**183.12**	**53.22**	**501.79**	**30.29**
3. Terpen compounds						
α – terpineol	0.05	ND	0.80	0.97	ND	0.05
Linalool oxide	0.05	0.05	ND	ND	ND	0.05
Nerol	0.05	ND	0.0006	0.11	ND	ND
β – citronellol	0.05	ND	0.17	0.19	ND	ND
Geraniol	0.05	ND	ND	0.17	ND	0.05
Total terpenes	**0.25**	**0.05**	**0.97**	**1.44**	**ND**	**0.15**
Total volatile compounds	**419.67**	**529.20**	**570.26**	**368.41**	**1202.55**	**394.35**

Twenty eight volatile compounds have been identified. The greatest variety of volatile compounds (22 identified) in red wine of the Rubin variety was found. The lowest content number (11 identified compounds) in the wine from Storgozia was established.

Considering the total content of volatile compounds, their lowest amount was found in the Trapezitsa wine (368.41 mg.dm^{-3}). The highest total volatile content was found in the Kaylashki rubin wine (1202.55 mg.dm^{-3}). This wine was distinguished from all others by the higher and significant amounts of volatile and aromatic components. The results for the total quantitative volatile composition of the wines examined were in absolute correlation with the data of other researchers [2].

The total amount of higher alcohols was lowest (101.48 mg.dm^{-3}) in the Rubin wine. This quantity was significantly lower compared to the results for this indicator in all red wines examined. The highest content of higher alcohols (504.84 mg.dm^{-3}) was found in the Kaylashki rubin wine. Immediately after it, according to this indicator, the wine of the Storgozia variety (427.63 mg.dm^{-3}) was ranked. The established total alcohols in the wines examined correlated with the presented data (up to 600 mg.dm^{-3}) of Chobanova, 2012 [11].

2-methyl-1-butanol (active amyl alcohol) and 3-methyl-1-butanol (isoamyl alcohol), higher alcohols found in all wines tested, were dominated. 3-methyl-1-butanol was represented with higher content. Its concentration was lowest for Rubin wine (37.19 mg.dm^{-3}). The highest was for Storgozia wine (273.63 mg.dm^{-3}). The isoamyl alcohol is one of the major components of the higher alcohols group. It gave typical notes of malt and whiskey in the wine aroma [19].This compound was one of those with an important aromatic effect found in the study of red wines of Merlot and Cabernet Sauvignon varieties produced in California and Australia [30]. A study of aromatic compounds in Cabernet Sauvignon wines during aging in stainless steel tanks found that 3-methyl-1-butanol was the main representative of higher alcohols occupying the largest quantity [13]. The obtained data on the presence of 3-methyl-1-butanol in the present study were in full correlation with the studies of the scientific groups discussed above.

2-methyl-1-butanol (active amyl alcohol) was found in the highest amount (68.14 mg.dm^{-3}) in the Kaylashki rubin wine. Immediately after it was the wine of Storgozia (66.11 mg.dm^{-3}). The lowest was its amount in Rubin wine (33.27 mg.dm^{-3}). According to Chobanova (2012) [11] the average content of this alcohol is about 36.00 mg.dm^{-3}.

2-phenylethanol was found in the Kaylashki rubin wine (133.13 mg.dm^{-3}) and Trapezitsa (11.59 mg.dm^{-3}). This alcohol is important to the sensory of the wine. It was identified in white and red wines from Northwestern Spain [14]. It was responsible for the aroma of rose in the wine [31].

A high content of 2-butanol has been identified. The highest was its quantity (87.79 mg.dm^{-3}) in Storgozia wine followed by Bouquet wine (69.56 mg.dm^{-3}). The lowest concentration (30.82 mg.dm^{-3}) of this higher alcohol in the Rubin wine was established.

1-pentanol was found only in Pinot Noir wine (31.45 mg dm^{-3}).

1-hexanol was identified only in the Kaylashki rubin wine, and 1-heptanol was found only in the Rubin wine. The last two alcohols were available in minor amounts.

A single aldehyde – acetaldehyde was identified in the wines studied. The highest was its amount in the wine of Kaylashki rubin (69.85 mg.dm^{-3}). In the wines of Storgozia, Bouquet and Pinot Noir it was found in very low quantities. The established acetaldehyde levels were normal for red wines.

The ester fraction was represented by 11 identified compounds. The esters were of fundamental importance to the complexity of the wine aroma. Very high total ester content (501.79 mg.dm^{-3}) was found in the Kaylashki rubin wine.This wine was characterized by the highest aromatic complexity. Immediately after it was the Rubin wine, where a total ester

content of 261.19 mg.dm^{-3} was established. The lowest overall concentration of esters (25.72 mg.dm^{-3}) in Storgozia wine was found.

The ethyl acetate was the main dominant ester. Its highest concentration (77.95 mg.dm^{-3}) was found in the wine of Kaylashki rubin variety. The lowest content of this ester (18.76 mg.dm^{-3}) in Trapezitsa wine was found. At concentrations up to 50.00 – 80.00 mg.dm^{-3} this ester provides a pleasant fruity aroma of the wine [11, 32]. At higher concentrations, its influence is negative [33]. The concentrations found in this study were in correlation with the above data, confirming the positive effect of ethyl acetate on the aroma of the wines studied.

With the highest amount of all identified esters isobutyl acetate was identified. This ester was found only in the Kaylashki rubin wine (273.23 mg.dm^{-3}).

The ethyl butyrate was found in the Rubin wine (83.74 mg.dm^{-3}) and in the Trapezitsa (0.05 mg.dm^{-3}). It was one of the esters with an important contribution to the fruit character of the wine [34]. It was also identified in Cabernet Sauvignon wines from China [32].

The isopentyl acetate was found only in the Rubin wine (156.85 mg.dm^{-3}). This ester was also established in Chinese Cabernet Sauvignon wines [32].

The ethyl caprylate was found in the wines of Rubin, Storgozia, Trapezitsa and Kaylashki rubin. Significant concentrations of this compound were found in the wines of the Kaylashki rubin (150.46 mg.dm^{-3}) and Trapezitsa (34.41 mg.dm^{-3}). Ivanova et al. (2013) [35] studied Macedonian and Hungarian wines and indicated higher amounts of ethyl caprylate in white wines than red wines.

The ethyl decanoate was identified in two of the wines – Bouquet (153.71 mg.dm^{-3}) and Rubin (0.05 mg.dm^{-3}). This ester was found to be a major in study on variations in the aromatic composition of Cabernet Sauvignon wines aging in stainless steel tanks [13].

Five terpene alcohols were found in the wines studied. The highest total amount of terpenes (1.44 mg.dm^{-3}) was determined in the Trapezitsa wine. The lowest total amount (0.05 mg.dm^{-3}) of these compounds was found in the Storgozia wine.

α-terpineol was identified in the Rubin, Bouquet and Trapezitsa wines. The highest was its content (0.97 mg.dm^{-3}) in the Trapezitsa sample, and the lowest (0.05 mg.dm^{-3}) in Rubin. α-terpineol was found to be one of the main terpenes in a Gewürztraminer wine [36].

Linalool oxide was identified in only three of the wines studied – Rubin, Storgozia and Pinot Noir. This compound was present in minor amounts.

Nerol was found in three of the wines studied – Rubin, Bouquet and Trapezitsa. The highest amount in Trapezitsa wine (0.11 mg.dm^{-3}) was established. The identified content of this terpen fully corresponded to its variance range (0.014 – 0.450 mg.dm^{-3}) presented by Chobanova (2012) [11].

β-citronellol has been identified in the Rubin, Bouquet and Trapezitsa wines. The highest was its concentration (0.17 mg.dm^{-3}) in the Trapezitsa wine. The content of this terpene in wines ranges from 0.014 – 0.450 mg.dm^{-3} [11], which fully corresponded to the concentrations obtained in this study.

The last identified terpene was geraniol. It was located in the wines of Rubin, Trapezitsa and Pinot Noir. The highest was its concentration in Trapezitsa wine (0.17 mg.dm^{-3}).

Another component of the volatile composition of the wine found in this study was methanol. This compound has no aromatic effect, but at high concentrations it is toxic. Its presence in wines is a normal phenomenon. Its presence is due to its precursor – fruit pectin, which is degraded to methanol from the pectolytic enzyme complex of the fruit [37]. The normal content of methyl alcohol in red wine ranges from 60.00 to 230.00 mg.dm^{-3} [16]. In this study this component of the volatile composition was found in all wines examined. The highest was its content in the Kaylashki rubin wine (126.07 mg.dm^{-3}), and the lowest in Rubin

wine (22.02 mg.dm^{-3}). The concentrations of this compound found in this study correlated with the range of its normal presence.

Conclusions

The conducted study for aromatic characterization of the volatile and aromatic composition of red wines from the region of Central Northern Bulgaria established:

- Twenty eight volatile compounds from different aromatic groups were identified and quantified. The largest species diversity of volatile compounds (22 identified) were found in the Rubin wine, and the lowest (11 identified) in that of Storgozia;
- The highest total volatile content (1202.55 mg.dm^{-3}) was found in the red wine Kaylashki rubin. This wine was with significantly higher content of volatile compounds than all others in the study;
- The highest total content of higher alcohols (504.84 mg.dm^{-3}) was found in the Kaylashki rubin wine. The lowest (101.48 mg.dm^{-3}) in the Rubin wine was found;
- 3-methyl-1-butanol (isoamyl alcohol) and 2-methyl-1-butanol (active amyl alcohol) were presented in all tested wines. The established higher alcohols with significant effect on the wine aromatic profile were also 2-phenylethanol, 2-butanol, 1-pentanol, 1-hexanol and 1-heptanol;
- Only acetaldehyde was found from the group of aldehydes. The highest was its content in the Kaylashki rubin wine (69.85 mg.dm^{-3});
- The ester composition of the wines was represented by 11 identified compounds. The red wine Kaylashki rubin showed high quantitative (501.79 mg.dm^{-3}) ester complexity.
- The presence of the ester ethyl acetate was predominant. The ester group has also been found to be ethyl butyrate, isopentyl acetate, ethyl caprylate, ethyl decanoate. These esters have a serious impact on the aromatic quality and complexity of the wines analyzed;
- The highest total terpene content (1.44 mg.dm^{-3}) was found in Trapezitsa wine. From this group of aromatic volatile compounds in the wines were found linalool oxide, nerol, α-terpineol, β-citronellol and geraniol;
- Methyl alcohol was found in the wines. Its amount ranged from 22.02 mg.dm^{-3} (in Rubin wine) to 126.07 mg.dm^{-3} (in the Kaylaski rubin wine). Its concentrations were normal for red wines.

The present study proved that red wines obtained from hybrid Bulgarian varieties (obtained by intra- and iter-species hybridization) were characterized by a complex and varied volatile composition similar to that of *Vitis vinifera* L.

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Determination of consistency of concentrated dispersed systems by the method of gravitational penetration

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Abstract

Introduction. Analytical and experimental studies consistency dispersion systems of the new method – gravitational penetration.

Materials and methods. Dispersion systems – pate meat products from mechanically separated poultry are being investigated. The consistency was determined by gravity penetration. Penetration indices are determined on the basis of mathematical modeling of indenter motion in the product layer based on second order differential equations of motion.

Results and discussion. The proposed method for determining consistency is easy to use. The presented calculus dependencies and mathematical models are based on physical constants, which makes the method of gravitational penetration versatile for wide practical application in estimating the quality of food by the express method. The presented mathematical model obtained based on the second-order differential equations, suitable for different research and use me different designs gravitational penetrometer.

To perform a comparative analysis of the consistency of food products obtained from different technological modes or formulations, it is proposed to use a comparative characteristic in the form of a coefficient K. Its value is calculated as the ratio of the depth of immersion of the needle into the product layer when falling penetrometer from one height.

The highest rates were pate sample containing 40% of mechanically separated poultry meat and 8% of rice flour, and the smallest, pate sample, containing 30% mechanically separated poultry meat and 10% of rice flour.

Conclusion. Defining the method of gravitational penetration extends the possibility of obtaining accurate results in comparison with the use of existing methods and a priori formulas.

Introduction

The penetration method is widely used for researching the consistency of structured foods. The experience with the practical application has confirmed the difficulty of getting unambiguous indicators of the force or other selected characteristics of the consistency obtained while even penetrometers and research methods of the same design are used. This is due to the measurement features embedded in their design and using the variety of mathematical calculation models [1, 2].

The modern penetrometers measure the magnitude of the force and the immersion depth of the indenter to determine the consistency of solid-like foods. Measurement is usually automatic. In this case, they use complex and, accordingly, cost-integrated electronic mechanical systems [3, 4].

To simplify the design of the penetrometer, which significantly reduces its value and obtain an accurate measurement result, adapted for different research conditions and properties of the studied materials, a simple gravitational method for determining the consistency of food-structured whole-piece dispersed systems is proposed. The new method is based on the fundamental laws of mechanics, which describe the motion of a solid material system (indenter) by gravity through a layer of material [5, 6].

For the universality of the research method, it is possible to use interchangeable indenters of various designs, and as a characteristic of consistency to determine penetration force, for example, using a needle working member, and penetration energy while using any other form of indenter [7, 8].

The purpose of the article is to promote and familiarize professionals with an innovative method of determining the consistency of concentrated food dispersed systems.

Materials and methods

Experimental device

During determining the consistency by the gravitational penetration method, it is measured the mass of the penetrometer, the height of its falling and the immersion depth of the indenter. These measurements are very simple and do not require any special equipment. The measurement sequence of the consistency of concentrated dispersed systems is shown in Figure 1.

Measurement order

Penetrometer in the form of a dart with a needle (indenter), tripod or other device for fixing the penetrometer at height, ruler for measuring the depth of the indenter, sample product.

The measurement sequence is as follows:

- the penetrometer is fixed with a tripod at a height H;
- a sample of product is placed on the bottom of the tripod on a porous substrate;
- release the mechanism of attachment of the penetrometer, which allows it to fall under the action of gravity on the surface of the sample;
- measure the depth of needle immersion;
- in the selected mathematical model for calculating the characteristics of consistency substitute the measurement data: m – penetrometer mass; H – drop height; y – immersion depth of the indenter into the product sample;
- calculate the consistency characteristics.

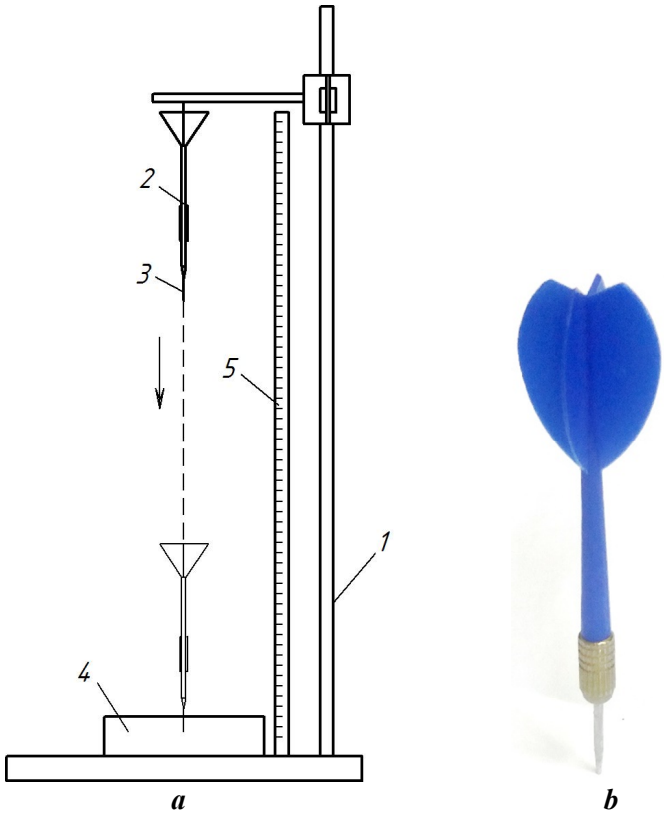

Figure 1. Experimental device:
a – experimental device; b – penetrometer;
1 – tripod; 2 – dart; 3 – needle; 4 – products; 5 – straightedge.

During the research to obtain reliable comparative indicators of consistency characteristics, it is necessary to use one-mass penetrometers with the indenters of the same shape and needle diameter and perform calculations according to one of the selected mathematical models, neglecting insignificant influencing factors on movement of the indenter in the product layer.

Investigated products

Changes in the structural and mechanical properties of a product that contains a different amount of mechanically separated poultry meat (MMV) are studied for recipes:

№2 – 30 %,
№3 – 35 %,
№4 – 40 %,
№5 – 45 %

and with rice flour addition:

№2 – 10 %,
№3 – 9 %,
№4 – 8 %,
№5 – 7 %

Results and discussion

Mathematical model of gravitational penetration

If in terms of product consistency characteristics, the vibration of the intension Fp movement resistance will be chosen, its magnitude could be found by using the motion differential equation of material system.

$$F_H + F_P = F_T, \tag{1}$$

F_H – inertia force, H; F_P – movement resistance force of the indenter, H; F_T – gravity, H.

In Figure 2 it is shown a diagram of penetrometer immersion in the product and power layer that are acting during this process.

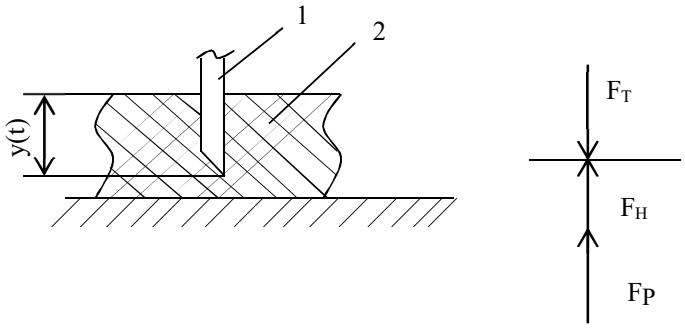

Figure 2. Scheme of penetrometer indenter immersion into the product layer and the forces acting on its motion:
1 – indenter needle; 2 – product.

Equation (1) is rewritten by revealing the magnitudes of forces.

$$m\frac{d^2y(t)}{dt^2} + F_p = mg \tag{2}$$

Consider the initial conditions: $t = 0, y(0) = 0; V(0) = \sqrt{2gH}$,

H –height, from which the penetrometer falls.

The equation solution (2) is written as follows:

$$y(t) = \frac{\left(mg - F_p\right)\cdot t^2}{2m} + V_0 t \tag{3}$$

From the equation (3) we find the resistance force of the indenter motion:

$$F_P = \frac{\left(t^2 g + 2V_0 t + 2y(t)\right)\cdot m}{t^2} \tag{4}$$

The analysis of the equation (4) shows that in order to determine the magnitude of the force F_P it is necessary to know the quantities: the initial velocity V_0, which is calculated from the equation $V_0=\sqrt{2gH}$; m – by mass of the penetrometer, which we find by weighing it; g – acceleration of the free fall of the body, which is a known physical constant g=9,8 м/с^2; $y(t)$ the immersion depth of the indenter, which is found by measuring the length of the needle in the product layer after stopping the movement of the penetrometer; t – duration of the needle immersion in the product layer, it is found by calculation after below mentioned analytical research of the material system mathematical model.

From the equation (3), we find the speed of the indenter.

$$\frac{dy(t)}{dt}=\frac{(mg-F_P)\cdot t}{m}+V_0 \tag{5}$$

At the end of indenter immersion, we have zero motion velocity. $\frac{dy(t)}{dt}=0$.

From the equation (5) we find t:

$$t=\frac{V_0 m}{F_P-mg} \tag{6}$$

With the use of equations (4) and (6) we can find the characteristic of the product consistency F_P. The calculation of the indenter movement duration includes the use of averaging movement velocity method, considering the linear nature of change in its immersion depth.

Time calculation scheme t.

In Figure 3 shows a chart of the motion velocity of the indenter depending on the depth of its immersion.

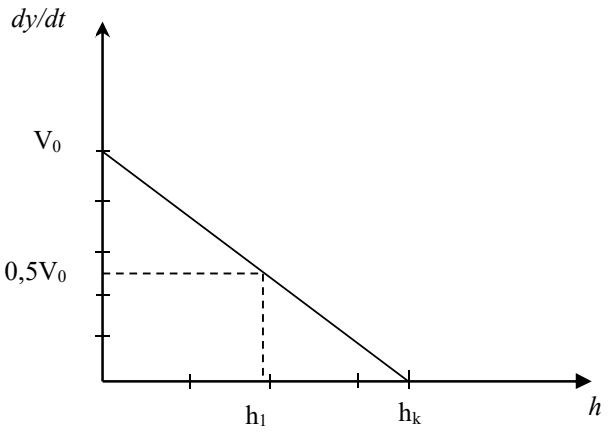

Figure 3. Chart of the motion velocity change *dy*/*dt* of the indenter depending on the depth *h* of its immersion

The indenter movement duration when it is immersed in the product at a depth of h_1, we find from the equation:

$$0{,}5V_0 = \frac{h_1}{t} \Rightarrow t = 2\frac{h_1}{V_0}$$

The method of proportions determines the duration of its motion to a stop when the immersion depth is h_k, so $t_k = h_k t_1 / h_1$.

The proposed method of determining the consistency of the product restricts the possibility of using penetrometers of different designs. A more accurate result can be obtained by refining the mathematical model – the differential equation of motion of the indenter, taking into account the dependence of the area of contact of its surface with the material [9, 10].

In this case, we can rewrite the differential equation as follow:

$$m\frac{d^2y(t)}{dt^2} + \pi D\mu_1\frac{dy(t)}{dt} - mg = 0 \qquad (7)$$

here D – the penetrometer needle diameter, m; μ_1 – the consistency characteristic, kg/m ×s.

Bear in mind that the consistency characteristics μ_1 and F_P have different units of measurement and different physical natures correspondingly.

Perform an equation analysis (7).

Equation solution (7) under initial conditions $t = 0$, $y(0) = 0$, $V(0) = V_0$ we have:

$$y(t) = \frac{m}{\mu}\left[\left(gt + V_0\right) + \frac{mg - V_0\mu}{\mu}e^{-\frac{\mu \cdot t}{m}} - \frac{mg}{\mu}\right], \qquad (8)$$

here $\mu = \pi D\mu_1$

Equation (8) has the same characteristics m, g, t, V_0 as equation (5). The difference is that in equation (5) the characteristic of the product consistency is the penetration force F_P, which has the unit of measurement N (Newton), whereas μ in equation (8) has the unit of measurement kg / s or N x s / m (Newton multiplied by a Second and divided by a Meter).

In food technology, there is a need for comparative analysis of the consistency of different foods. It occurs mainly when a product is adopted as standard and needs to be defined as a new product or obtained from different technological modes or formulations, differing in their consistencies [11, 12].

In this case, it is quite enough to measure the immersion depth of indenter in the product. The use of penetrometers with the same design and mass, and falling them from the same height are prerequisites for such studies.

The ratio of different values of the needle indenter immersions in the product is a comparative characteristic of the consistency of the product.

It is the index $K = \frac{H_S}{H_{pr}}$, here H_S – the immersion depth of the penetrometer needle into the product which is adopted as standard; H_{pr} – the immersion depth of the penetrometer needle into the test product.

When K> 1, we have a product of a harder consistency. And on the contrary, if K< 1, we have a product of a softer consistency.

Determination of structural and mechanical properties of meat products

Changes in the structural and mechanical properties of a product that contains a different amount of mechanically separated poultry meat (MMV) are studied (recipes №2 – 30 %, №3 – 35 %, №4 – 40 %, №5 – 45 % correspondingly) with rice flour (recipes №2 – 10 %, №3 – 9 %, №4 – 8 %, №5 – 7 % correspondingly).

The data of experimental studies of the indenter immersion depth into the pate are shown in Figure 4.

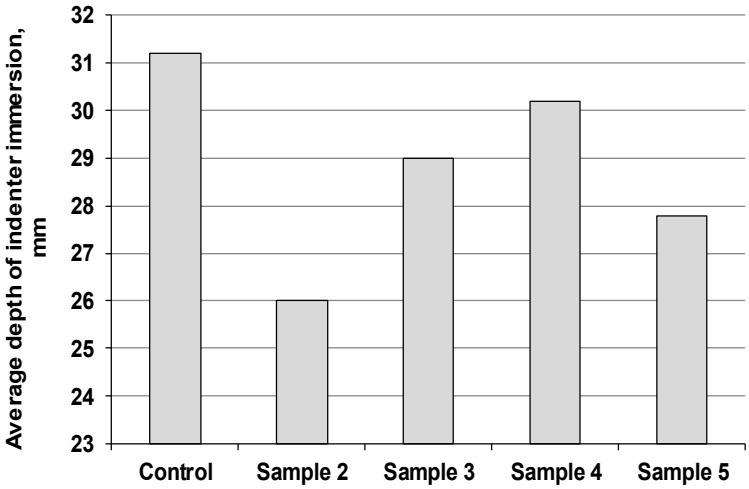

Figure 4. Indenter immersion depth into pate with MMB and rice flour

As a result of the research of the immersion depth of the indenter in the meat pate samples, the following data was revealed: in the control sample, the immersion depth of the indenter was – 31,2 mm, whereas the indices for samples containing MMV and rice flour were: №2 – 26,0; №3 – 29,0 mm; №4 – 30,2 mm; №5 – 27,8 mm. The lowest immersion depths of the indenter were ones for sample №2 containing 30 % MMB and 10% rice flour. So we can say that that the index of its consistency has K> 1, it is equal to K = 1,2.

The analyisis of the obtained data indicates that the including MMV and rice flour in the paste mass contributes to a slight change in the consistency of the product.

The results of the theoretical investigation of the movement of a material object in the form of indenter through the product layer are presented. There is a certain sequence of the consistency of the product, its mathematical model in the form of a second order equation. The solution has been found on initial terms which take place when using the gravitational characteristics of falling penetrometer from a predetermined height.

The sequence of execution of researches is given and the features of use of the needle indenter are shown.

For a comparative analysis of the consistency of similar products we have the possibility to determine its level of change by calculation the ratio of the indenter penetration depth. In the case when the ratio of penetration depth of certain product, adopted as a standard with its consistency, to the penetration depth of the tested one (it can be produced by new technology)

is less than one it means the consistency is considered too hard. And on the contrary, if the ratio exceeds one it means that its consistency is too soft [13, 14].

The proposed method for determine the consistency of food is an alternative to widespread method with the use of electronic mechanical devices with wide range of indenters of different constructions (conical, needle or spherical).

Conclusion

Conducted research and received mathematical data let think that this proposed research method of structuring food consistency by gravitational penetration with the use of the needle indenter is competitive comparing with the best worldwide analogs of express measurement.

Its distinctive feature is simplicity of constructive content and at the same time it has scientific point that relies on the classical laws of material systems [16].

Comparing to existing methods of measurement of consistency and defining some efforts of penetration the mathematical models of movement of material systems with applying second order differential equations were used. This fact expands significantly the ability of obtaining exact results comparing to the use of previous formulas, for example during conducting research on conical indentometers.

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Effect of the traditional koumiss yeast produced in Turkey on some properties and carbonyl components of koumiss

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Abstract

Introduction. Koumiss produced from different types of milk (horse, cow and goat milk) by traditional koumiss yeast and observe the changes of aroma components and biogenic amines formations during the storage period (30 days) are presented in this work.

Materials and methods. Mare milk was used directly but the composition of cow and goat milk is different from that of mare milk, the compositions of these milk were used in the production of koumiss by emulating mare milk. Koumiss were produced with traditional yeast. Biogenic amine analysed with high performance liquid chromatography and aroma components was determined by headspace-gas chromatography.

Results and discussion. The lactic acidity value (%) has gradually increased during the storage period of koumiss samples. The highest amount of ethyl alcohol was determined in koumiss (30^{th} day) produced from cow milk (1.95%). Among the biogenic amines, the value of putrescine was found to be highest in koumiss produced from goat milk (5.68–5.86 ppm), while the cadaverine value was observed to reach to the highest values (2.66–9.74 ppm) in koumiss produced from horse milk. The amount of tyramine increased significantly in all koumiss samples. Phenyl ethylamine was determined only in goat milk koumiss (0.64–0.84 ppm). The histamine value was observed to be at the highest ranges in the horse milk koumiss (4.80–6.52 ppm).

The aroma values on first day of storage in koumiss samples were determined as 0.78–3.76 ppm acetaldehyde, 0.23–0.27 ppm acetoin, 0.80- 1.62 ppm diacetyl, 0.03–0.06 ppm methanol, 7.27–14.73 ppm butyl butyrate, 1.31–11.86 ppm ethyl acetate. No statistically significant difference was found between the aroma substances in terms of milk type.

Conclusions. Biogenic amines in koumiss produced by traditional koumiss yeast with different types of milk in Turkey were below the acute toxicity doses. In terms of aroma substances, milk types was has the same effect on aroma substances statistically.

Introduction

Koumiss is an old Turkish drink produced of mare milk having fragrant, sourish, light foamy, refreshing qualities and it is called as "Kumys", "Koumiss", "Kumiss" in the literature of different countries [1]. Traditional koumiss yeast in nomadic life at the end of the lactation period of the mares by adding goat milk into the leather bottles of koumiss and it is conserved until the next lactation period. When the mares begin to be milked, koumiss yeast is obtained by adding mare milk into the leather bottles in small amounts for five days [2].

When various properties of koumiss obtained from mare milk are examined; pH 7.03, titratable acidity (0.05%), density 1.033 g/cm3, lactose 6.10–6.37%, dry matter 10.20–11.80%, fat 1.21–1.90%, protein 2.14–2.70%, ash 0.42–0.50% alcohol amount 0.5–2.5% were observed [2,3]. It was determined that not only the lactose ratio decreases but also protein ratio decreases since proteins break the longer koumiss is stored. It is determined that also a significant decrease in specific gravity takes place too. However, it was determined that acidity and alcohol content had increased [4].

Cow milk and mare milk differ significantly in terms of composition. Mare milk is richer than cow and goat milk in terms of lactose content. Since cow, sheep, goat milks are not suitable to produce koumiss, using them by emulating mare milk has been reported to be appropriate [5,6]. Cow milk has been tried to make suitable for koumiss production by adding water, whey, glucose or saccharose, ascorbic acid in different ratios to increase sugar content, by reducing fat content of cow milk or using membrane technologies [6,7].

Aroma of koumiss is originated from compounds such as propyl alcohol, butyl alcohol, propionic acid, glycerine, aldehydes, acetone, various esters and volatile acids resulting from fermentation of lactic acid and alcohol [3]. Esters are formed from the reaction between organic acids and alcohols in koumiss. Traditional koumiss yeast due to containing lactic acid bacteria and yeasts, there may be differences at the taste and aroma formation in the product [8,9].

The aim of this study is to determine the chemical properties, aroma substances and biogenic amine contents of the koumiss samples produced by using traditional koumiss yeast of horse, goat and cow's milk throughout its storage period. Determine the effect of milk types on the aroma substances of koumiss. In addition, observing the biogenic amine formations that cause carcinogenic toxic poisoning and the effects of milk species diversity in the traditional koumiss are among the objectives of this study.

Materials and methods

Materials

Koumiss Production

Preparation of mare, cow and goat milk. Mare milk was used directly for the production of koumiss without separating its fat. Since the composition of cow and goat milk is different from that of mare milk, the compositions of these milk were used in the production of koumiss by emulating mare milk. In order to simulate mare milk, fat of cow and goat milk was adjusted according to the composition of mare milk (0.5%). Then 2.5% lactose (ENKA Dairy A.Ş. in Konya/Turkey) was added to these milk types.

Preparation of koumiss yeast. The traditional koumiss yeast obtained from İzmir Alaş Koumiss Production Farm – İzmir/Turkey has been used as bulk culture. For the preparation of yeast, 2–3 minutes heat treatment at 90–92 °C was applied to the mixture added 90% water, 3.2% milk powder, 5.8% whey powder and 1% lactose. It was stirred by adding traditional koumiss bulk culture of 150–200 ml cooling to room temperature with the pH value 5.6–5.7. Koumiss were incubated for 16 to 17 hours at 22 °C. until pH value 4.4–4.5 and stored in the refrigerator. One day later it was used as koumiss yeast.

Production of koumiss. The same procedures were applied to all types of milks used at testing. Firstly, mare, cow, and goat milk were pasteurized for 30 minutes at 70 °C. Then, 10% of koumiss starter culture at 28–30 °C was added to milks cooled at 30 °C. At the 1st hour following the start of fermentation, first stirring was carried out around 5–10 minutes. After then the stirring procedure was applied for 1–2 minutes at every other hour until the pH was 4.8. The last 5 minutes of stirring was carried out when pH was 4.8. By filling in bottles at this pH, the product was cooled to 4°C and stored at the same temperature. Koumiss were stored at the refrigerator temperature for 30 days and analysis were carried out on the 1st, 15th and 30th days.

Chemical analysis of raw milks and the koumiss

Analysis of raw milk and koumiss were determined according to the total dry substance method described in [10]. Milk fat was determined using gerber method [11]. Specific gravity was determined with volumetric pycnometer (Glass Tube, 10 mL, Istanbul, Turkey) [12]. Titration acidity in raw milk and koumiss were determined as lactic acid % according to the method of AOAC [13]. While pH was measured with pH meter (WTW pH 3110, Germany). Alcohol content was prescribed with pycnometric method [14].

Biogenic amine analysis

Sample preparation. After 50 ml of the samples were homogenized for 15 minutes with 50 ml of 0.2 M hydrochloric acid, the mixture was centrifuged at 2150 rpm for 30 minutes. In the sample cooled to 4 °C, the separated phase at the top was collected. The sample filtered from Whatman 42 filter paper was derivatized before being analysed with High Performance Liquid Chromatography (HPLC) [15].

Derivatization. 400 mL to the sample, 400 ml N_2CO_3 (2g/100 ml H_2O) and 400 ml densyl chloride (10 mg/1 ml acetone) added 40 ºC incubated in water bath for 30 minutes. 200 ml Na-L-glutamate monohydrate (200mg/4 ml H_2O) is added to the solution and incubated at the same temperature for another 1 hour. After incubation, 1 ml of acetonitrile is added to the mixture and centrifuged at 2500 rpm for 10 min. Supernatant liquid is removed and injected to HPLC.

Characteristics of the chromatography device used. A diode array detector (220 nm), pump (LC – 10Advp), system controller (SCL – 10Avp), Degasser (DGU – 14A), Column oven (CTO – 1 CVp) and column (Prodigy 5m A Shimadzu HPLC device with ODS (2) (250 x 4.6 mm) was used for biogenic amine analysis.

Chromatographic conditions. The column temperature of the HPLC device was set at 30 °C and the flow rate to 1.0 ml/min. For the mobile phase, buffer (pH 8) was prepared using 0.1 M tris, 0.1 M acetic acid and water in 2: 1: 2 ratios, respectively. To prepare solvent A; 30 ml buffer, 550 ml acetonitrile, 420 ml distilled water were used. Solvent B was prepared by mixing 2 ml of buffer, 900 ml of acetonitrile and 100 ml of distilled water.

Aroma components analysis

Analysis of the aroma components was determined by gas chromatography (GC) [16]. The sample was put in the headspace vial and analysed.

Properties of the chromatography device used: GC/MS (Gas Chromatography, mass spectrometry), the oven was kept at 35 °C for 2 minutes, the temperature was increased to 240 °C with an increase of 5 °C/min and kept at 24 °C for 20 minutes. CP WAX (50m x 0.32 id) was used as the column. The injection temperature was set to 180 °C. The detector temperature is 200 °C.

Headspace conditions: Headspace sampler parameters are as follows: head pressure 27 psi, 5 min. thermostat time, 90 °C needle temperature, 120 °C transfer line temperature, 0.5 min of pressurization time and 0.08 min of injection time [16].

Microbiology analysis

The count of total aerobic mesophilic bacteria count was conducted according to Plate Count agar (PCA) [17]. Incubation was performed at 35 °C for 48 h., yeast-mold count according to Dicloran Rose Bengal Chloramphenicol agar (DRBC) (at 25 °C for 3 – 5 days) and total coliform bacteria (at 37 °C for 48 h.) counting according to Davis [18].

Statistical analysis

Variance analysis was performed to determine whether milk types had any effect on the samples examined or not. Duncan Multiple Comparison Test was applied to the results with the purpose of determining the effect of different effect from the main variation sources [19]. Statistical analysis was performed using SPSS 17.0 program [20].

Results and discussion

Chemical properties of raw milk used in koumiss production are shown in Table 1.

Table 1

Characteristics of raw milk used in koumiss production

	Raw horse milk	Raw cow milk	Raw goat milk
Dry-matter (%)	10.58±1.24*	8.72±0.33	9.40±0.28
Specific gravity (g/cm^3)	1.031±0.00	1.031±0.00	1.038±0.00
pH	7.00±0.15	6.79±0.14	6.80±0.01
Lactic acid (%)	0.05±0.00	0.16±0.01	0.17±0.02
Fat (%)	0.50±0.01	3.20±0.01	4.55±0.02

*Standart Deviation

While fat free dry substance content of horse milk was found as 10.58% this value was determined as 9.40% in goat milk. The specific gravity of cow and horse milk was determined 1.031 g/cm^3, while goat milk had 1.038 g/cm^3. The pH of the goat milk was found as 6.80 and pH of the horse milk was 7.00. It was observed that the lactic acid level of horse milk

was 0.05% and cow milk was higher (0.16%). Fat content of goat milk was determined as 4.55%, while cow milk was 3.20% and horse milk was 0.50%.

Küçükçetin [5] in his study determined horse, goat and cow milk specific gravity values respectively 1.034 g/cm^3, 1.035 g/cm^3 and 1.038 g/cm^3 whereas pH values of horse, goat and cow milk as 6.98, 6.18, 6.71. Lactic acid (%) values were determined as 0.08% in horse milk, 0.18% in cow milk and 0.14% in goat milk. While dry substance values of horse milk were found between 10.1% and 11.4%, it was determined that the dry substance value of modified cow milk as 9.15%. In studies conducted fat values of cow and goat milk were determined respectively as 1.21%, 3.61% and 4.10% [21,22,23]. The raw milk analysis findings of the researchers show similarity with this study.

Chemical analysis results in koumiss

Chemical properties of koumiss samples during 30 days storage are presented in Table 2.

Table 2

Chemical results of koumiss which is produced from different types of milk in different periods of storage

Chemical Analysis	Samples	Storage Periods		
		1 day	15 day	30 day
pH	A	4.47±0.14	3.43±0.35	3.22±0.17
	İ	4.63±0.04	3.46±0.29	3.30± 0.21
	K	4.55±0.23	3.53±0.39	3.37±0.16
Lactic acid value (%)	A	0.56±0.04	1.20±0.54	1.92±0.27
	İ	0.73±0.09	1.33±0.31	2.05±0.24
	K	1.02±0.08	1.53±0.45	2.28±0.19
Specific gravity value (g/cm^3)*	A	1.034±0.00^{bB*}	1.031±0.00^{bB}	1.028±0.00^{bA}
	İ	1.037±0.00^{bB}	1.033±0.00^{bB}	1.030±0.00^{bA}
	K	1.040±0.00^{aB}	1.038±0.00^{aB}	1.038±0.00^{aA}
Dry-matter (%)*	A	9.04±0.57^{bB}	9.02±1.06^{bB}	8.31±1.33^{bA}
	İ	10.48±1.04^{bB}	9.40±1.93^{bB}	8.40±1.51^{bA}
	K	12.40±0.95^{aB}	11.45±0.20^{aB}	10.67±0.92^{aA}
Ethyl alcohol value (%)*	A	0.69±0.36^{aC}	1.22±0.06^{aB}	1.52±0.88^{aA}
	İ	0.85±0.50^{aC}	1.34±0.12^{aB}	2.11±0.39^{aA}
	K	0.64±0.32^{aC}	1.36±0.20^{aB}	1.95±0.26^{aA}

*Difference between groups have determined that significant showed as small letter. Difference between times have demonstrated that significant showed as capital letter ($p<0.01$), A: Koumiss which is produced from horse milk, İ: Koumiss which is produced from cow milk, K: Koumiss which is produced from goat milk

It was determined that the pH value decreased in all koumiss samples during the storage period. The pH value of the milk produced by horse milk was determined as 4.47 on the 1st day of storage. It was found that the pH value decreased at the end of storage. While the pH value was observed as 4.63 on the 1st day of the cow milk used in koumiss, the pH value was decreased as 3.30 at the end of the storage. When the pH values of the koumiss were examined, it was observed that the effect of the type of milk and the change in storage time was not significant ($p<0.01$).

In Küçükçetin et al. [7] study, the pH of koumiss produced of modified cow and mare milk on day 1 of the storage was determined as 4.60. Whereas on the 15th day, the pH values were 4.41 and 4.33, respectively [7]. The pH values were found to be lower than the results of this study.

It was determined an increase at the lactic acid values of all koumiss samples during the storage period. The highest lactic acid value (2.28%) is observed in koumiss produced of goat milk at the end of the storage. The 1st day lactic acid value (0.56%) of koumiss sample produced of horse milk was determined to be at the lowest level. Akuzawa and Suruno [24] reported that the lactic acid content of koumiss was between 0.6% and 1.0%. The lactic acid values % of all samples were slightly higher than the results reported by the researchers.

The specific gravity of koumiss produced of horse milk was 1.034 g/cm^3 on 1st day, it was observed that it dropped to 1.028 g/cm^3 value on 30th day. This values are 1.037 g/cm^3 and 1.030 g/cm^3 at the koumiss produced of cow milk, respectively. The values found in koumiss that goat milk used in its production were found as 1.040 g/cm^3, 1.038 g/cm^3 respectively. It was determined that milk type and storage duration have statistically significant effect on specific gravity values ($p<0.01$).

In a study on the properties of koumiss produced by using traditional koumiss yeast, it was determined that the specific gravity values of koumiss samples decreased during the storage period [25]. It is found that the koumiss study bear a resemblance from this aspect.

The dry substance ratio of the horse milk koumiss samples during storage was determined as (8.31–9.04%). Dry substance values of koumiss show similar values with result of the study of Kınık et al. [26].

Although the type of ethyl alcohol contained in the samples did not significantly affect the type of raw milk, the difference between the times was found to be statistically significant ($p<0.01$). The lowest ethyl alcohol content (0.64%) was determined in the goat milk koumiss sample while the highest value (2.11%) was found in the cow milk koumiss sample.

Choi [27] found ethyl alcohol ratio in the product known as airag similar to koumiss produced of mare milk in Mongolia between 1.44–2.57%. In koumiss studies produced of mare milk, the ethyl alcohol values were found to be between 0.7–2.6% [24,28,29].

Biogenamine results of koumiss

The amount of biogenic amines that koumiss samples contain during milk storage according to their milk types are shown in Table 3.

It is reported that as a result of interaction between microbial flora present in starter culture causes and normal microbial flora in milk causes directly or indirectly the formation of biogenic amines [30]. It has been shown that the types of milk used in production and the pasteurization temperature applied to milk also affect the formation of biogenic amines [31].

Table 3

Biogenic amine values (ppm) of koumiss which is produced from different types of milk in different periods of storage

Biogenic Amine Values	Samples	Storage Periods		
		1 day	15 day	30 day
Putrescine	A	4.33±0.46	2.60±0.55	4.21±1.25
	İ	3.90±0.94	4.75±0.93	4.65±0.95
	K	1.09±0.37	5.86±4.83	5.68±4.92
Cadaverine	A	9.74±1.16	2.66±1.40	4.00±1.07
	İ	3.47±0.29	3.01±1.38	1.70±0.53
	K	4.64±3.54	5.76±3.56	4.42±3.92
Histamine*	A	$4.80\pm0.12^{aA*}$	5.51 ± 1.08^{aA}	6.52 ± 0.06^{aB}
	İ	4.55 ± 0.29^{bA}	4.67 ± 0.18^{bA}	4.90 ± 0.18^{bB}
	K	3.77 ± 0.60^{bA}	4.70 ± 0.17^{bA}	4.86 ± 0.40^{bB}
Tyramine	A	1.88±0.07	12.48±10.21	29.15±4.35
	İ	1.84±0.16	13.08±6.71	23.85±0.45
	K	2.14±0.31	23.71±17.39	27.40±5.90
Tryptamine	A	ND	ND	ND
	İ	ND	ND	ND
	K	ND	ND	ND
2-Phenylethylamine	A	ND	ND	ND
	İ	ND	ND	ND
	K	ND	0.84±0.72	0.64±0.20

*Difference between groups have determined that significant showed as small letter. Difference between times have demonstrated that significant showed as capital letter ($p<0.01$), A: Koumiss which is produced from horse milk, İ: Koumiss which is produced from cow milk, K: Koumiss which is produced from goat milk; ND: Not detected.

Some polyamines (such as putrescine, spermidine, spermine and cadaverine) are indispensable components for living cells. Nucleic acid functions and protein synthesis is also important in the regulation of cell membrane since they play a role in the stabilization [32,30]. Although putrescine and cadaverine have no direct toxic effect, they have been indicated to increase the toxic effects of other amines. It has also been reported that putrescine and cadaverine can produce carcinogenic compounds by reacting with nitrite [30,33].

When samples of koumiss obtained from different milk samples were examined, it was observed that milk type and storage time were not significant in putrescine values ($p<0.01$). Although the putrescine values of the koumiss produced of horse and cow milk were close to each other on the last day of storage, the putrescine value of koumiss produced of goat milk sample was found to be approximately 1 ppm higher. At a study conducted by Til et al. [34] on mice, acute toxicity dose for putrescine some orally taken biogenic amines causes was determined as >2000 mg/kg. When the putrescine values in the study were examined, it

was observed to be lower than the acute toxicity dose Til et al. [34] determined in their own study.

The koumiss samples produced of goat and horse milk was found that the highest level cadaverine (4.42 ppm, 4.00 ppm, respectively). But the lowest level (1.70 ppm) was determined in the koumiss samples produced of cow milk. The toxicity dose caused by cadaverine was reported to be >2000 mg/kg [34,30]. From the reported toxicity dose, the cadaverine levels of all the samples in the study were found to be lower.

Histamine is a chemical that exhibits strong biological activity. It stimulates cardiovascular system, uterus, intestine and smooth muscles, respiratory tract, sensory motor neurons in the body and controls gastric acid secretion. Histamine poisoning may occur due to the consumption of foods containing high levels of histamine [35]. The toxic dose for histamine is reported to be >1000 mg/kg. The critical dose of oral histamine is estimated to be between 100 and 200 mg [36]. In the study, histamine level at the end of storage in koumiss samples produced of horse milk determined as 6.52 ppm. This value is observed to be below the critical dose of oral histamine reported by of Aygun et al. [36].

Thyamin is an important biogenic amine whose antioxidative activity increases due to the amount it contains [37]. Like histamine and serotonin also tyramine is one of necessary amines in the operation of nerve system and control of blood pressure. Like histamine and phenylethylamine also tyramine is among the amines having the highest toxic effect. 100 – 800 mg/kg values for tyramine have been reported as toxic doses in foods [35,38,39,40]. When the tyramine values were examined in this study, it was observed that the samples of koumiss produced of horse milk had the highest tyramine (29.15 ppm) value at the end of the storage. Küçükçetin [5], determined increase in tyramine levels during storage period. He also determined that koumiss samples produced of mare milk contain more tyramine than the ones produced of cow milk. It has similar characteristics with the findings of the study.

It is known that tryptamine has an elevating effect on blood pressure [41]. No tryptamine was detected in none of the samples during storage.

During storage, 2-phenylethylamine content was not found in horse and cow milk koumiss samples, but determined in goat milk koumiss sample. It has been reported that 2-phenylethylamine taken from foods in individuals sensitive to migraine attacks can trigger migraine attacks and increase blood pressure. The toxic dose for 2-phenylethylamine was determined as 30 ppm [42,43]. The maximum amount of phenylethylamine determined in the study was determined as 0.84 ppm. It has been observed that this level not causing any toxicity.

Özdestan and Üren [44] reported that they did not detect 2-phenylethylamine content on the 7th day of storage of 10 different kefir samples. Phenylethylamine was not detected on 1st day of the koumiss samples.

Aroma Substances Result of Koumiss

Some carbonyl components of the koumiss samples are shown in Table 4.

The highest acetaldehyde value (3.97 ppm) during storage was determined on the 30th day of the horse milk koumiss sample.

According to the research of Topuz [25], the effect of different fermentation durations on the development of acetaldehyde was reported to be statistically different from each other. Differences in the amounts of acetaldehyde in storage period of samples of koumiss were also observed.

Table 4

Aroma substances results of koumiss which is produced from different types of milk in different periods of storage

*Aroma Substances	Samples	Storage Periods		
		1 day	15 day	30 day
Acetaldehyde (ppm)	A	3.76±3.45	2.66±2.29	3.97±1.07
	İ	1.62±1.41	1.81±1.03	1.19±0.20
	K	0.78±0.68	7.93±5.76	1.06±0.10
Acetoin (ppm)	A	0.27±0.06	0.29±0.04	0.10±0.18
	İ	0.23±0.00	0.22±0.002	ND
	K	0.23±0.19	0.28±0.06	ND
Diasetil (ppm)	A	0.80±0.58	1.46±0.49	1.97±1.19
	İ	1.62±1.05	1.62±0.10	2.58±0.93
	K	0.90±0.52	1.32±0.49	1.45±0.55
Metanol (ppm)	A	0.06±0.11	0.13±0.23	8.84±3.55
	İ	ND	ND	12.87±5.17
	K	0.03±0.05	ND	11.44±5.67
Butilbutirat (ppm)	A	7.65±2.38	12.17±6.98	5.41±9.37
	İ	14.73±8.40	16.01±0.92	12.32±10.67
	K	7.27±4.49	11.56±2.88	6.87±3.05
Ethylacetate (ppm)	A	11.86±11.27	9.15±8.27	0.61±0.16
	İ	2.66±2.23	7.17±5.70	0.31±0.06
	K	1.31±0.79	30.73±29.28	0.29±0.07

* A: Koumiss which is produced from horse milk, İ: Koumiss which is produced from cow milk, K: Koumiss which is produced from goat milk; ND: Not detected.

At the end of storage (30th day) it was observed that no acetoin detected in cow and goat milk koumiss, the amount of acetoin (0.10- 0.29 ppm) horse milk koumiss at the end of storage. Güzel-Seydim et al. [45] reported in their study that while the amount of acetoin of kefir on the 1st day was 25 µg/g, decreased to 16 µg/g on the 21st day of the storage. It shows similarity to koumiss study in terms of decrease in acetoin amount at the end of the storage.

When diacetyl values were examined, a slight increase was generally observed during the storage period. The highest amount of diacetyl was found in the sample of cow milk koumiss. The highest diacetyl (1.45- 2.58 ppm) values were reached on the 30th day of storage.

Topuz [25] found that diacetyl amount as 6.52 ppm on first day 6.86 ppm on day 7, 6.37 ppm on day 14 and 5.42 ppm on day 21 in koumiss produced of traditional culture.

The amount of methanol in all koumiss at the end of storage was determined to be between 8.84–12.87 ppm. Magalhães et al. [46] reported that methanol as being highly toxic. According to Ethylalcohol Council Regulation (EECNo. 1576/89) the maximum legal limit is set as 1000 ppm [47]. The values found in all koumiss samples were obderved to be well below the legal limit.

The highest butylbutyrate (16.00 ppm) content was found on the 15th day of storage in the sample of cow milk koumiss. Esters are produced through fermentation by microorganisms including bacteria, molds and yeasts such as lactic acid bacteria. Ester

synthesis is obtained by the esterification and alcoholysis reactions of short and medium chain fatty acids and alcohol catalyzed by esterase, lipase and alcohol alkyltransferase. Esters commonly found in fermented dairy products and milk; defined as etheric, sweet, fermented and yeast produce a fruit-like aroma of such as apple, banana, pear, pineapple [48]. The lowest butylbutyrate (5.41 ppm) content was found in the sample of horse milk koumiss at the end of storage.

Ziino et al. [49] found the ethyl acetate value as 176 on the 30th day of ripening in cheese. In their study, among esters only ethyl acetate reached a high concentration after 7 days and increased rapidly [49]. When koumiss study was analyzed in terms of ethyl acetate content, the highest value (30.73 ppm) was determined on the 15th day storage of sample of goat milk koumiss. The lowest ethyl acetate content (0.29 ppm) was found at the end of the storage period of sample of goat milk koumiss.

Conclusion

According to the findings obtained, it was determined that biogenic amines (putrescine, histamine, cadaverine, tyramine, tryptamine and phenylethylamine values) in koumiss produced of horse milk, goat milk and cow milk were below the acute toxicity doses. However, it was observed that the histamine value reached to a higher value at the end of storage in koumiss produced of horse milk. Histamine value was found to be statistically differ according to milk type ($p<0.01$). Among the aroma substances; acetaldehyde, acetoin, diacetyl, methanol, butylbutyrate, ethyl acetate values were found to have no effect on the milk type.

Although horse milk is the most suitable milk for the production of koumiss, it is thought that due to being economical and healthy, the modified cow and goat milk can be used for the production of koumiss when needed.

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Efficiency of using of the mineralized malts composition for the enhancement of food products by micronutrients

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Abstract

Introduction. The purpose of research is to obtain and investigate the composition of malts with high content of deficient micronutrients and enrichment with selected raw materials the rye-wheat bread.

Materials and methods. To obtain mineralized grain raw materials, maize and oat were germinated using solutions of zinc salt (ZnSO4) and chromium one ($CrK(SO_4)_2 \times 10H_2O$) of different concentrations: 0.001%, 0.002%, 0.003%, 0.004%, and 0.005%. X-ray fluorescence analysis was used to determine the mineral composition of grain and malt and stripping voltammetry method to determine the zinc content.

Results and discussion. The optimum concentration of zinc salt in soaking water equaled 0.002%, at which the zinc content of the enriched maize increased by 6.7 times compared to the original grain. For the enrichment of grain with chromium ions, the chromium salt concentration in soaking water should not exceed 0.001%.

According to the X-ray fluorescence analysis the mineral content in enriched malt is increasing, the content of zinc increased by 6 times in comparison with the original, and content of chromium by 3 times, that indicate the possibility of the source raw material mineral composition correcting by soaking and germinating grain in aqueous solutions of microelement salts.

To enrich the food products with mineralized malts, rye-wheat bread was chosen as the traditional product in this work. Mineralized malts have a positive effect on the lifting power of yeast, and more so when zinc salts are added. This indicates a reduction in the duration of the technological process.

Studies of influence of the inserted mineralized malt's weight part on the quality indicators of rye-wheat bread showed that the optimal amount is the introduction of 10% by weight of flour.

Conclusions. The addition of such mineralized raw materials to food products formula will enrich them with biologically active substances gives them functional properties.

Introduction

Functional food products based on fermented beverages are being developed most dynamically in the world market, and are based on fermented beverages and bakery products [1, 3, 4, 8, 9, 10].

Unlike many other products, bread products are able to provide the human body with a large amount of energy and almost all vital substances: proteins, carbohydrates, vitamins, minerals. Nutritional value of bread depends on the type and kind of flour, recipe additives and humidity of the product.

Compared to wheat flour products, rye bread differs favorably in the content of essential amino acids, minerals and vitamins. Therefore, having a lower energy value than wheat bread, it has a higher biological value, that is, it better provides the human body with the necessary substances [11, 12, 13, 14]. Despite the high nutritional value, according to the modern requirements of the nutrition science, bread products need to improve their composition. Bread do not have the optimal ratio of proteins and carbohydrates, calcium and phosphorus, insufficient micronutrient content, essential amino acids such as lysine, methionine, tryptophan.

The enrichment of food products, in particular the bakery products with high micronutrient content, is an urgent task. It is known that deficiency of micronutrients, especially such as zinc, chromium, selenium and others, today there is an acute issue [2, 5, 7, 15, 16, 17, 18]. The deficiency of microelements reduces the body's resistance to various diseases, accelerates the aging process, increases the negative impact of adverse environmental conditions, and prevents the formation of a healthy generation [6, 19, 20, 21, 22].

Systemic usage of malt stimulates metabolism and hematopoiesis, strengthens the immune system, compensates for vitamin and mineral deficiency, improves acid-base balance, and promotes intense digestion. When choosing malt composition, we were guided by the fact that the composition of these types of malt based on maize and oat makes it possible to exceed the shortage of certain valuable nutrients. Thus, vitamin E is found in maize malt in large quantities, while oat malt is rich in threonine and lysine, but lysine is deficient in wheat flour. Oat malt is especially valuable for its macro- and microelement content; while maize is the source of vitamins and the main raw material for the production of diet products.

It is known that it is expedient to carry out cereals mineralization by germination in the mineralized medium. Actually this method of grain processing that metal ions are incorporated into organic complexes that are easily digestible for the human body [23, 24, 25, 26].

The microelements are actively involved in the enzymatic processes that take place in the grain, promote its growth and development and are important in the functioning of the human body. Chromium is important for the prevention of diabetes and cardiovascular disease; it also regulates carbohydrate metabolism and blood glucose. Zinc shows immunomodulatory, anti-inflammatory, antimicrobial, antioxidant functions. It affects the activity of hypophysiotropic hormones, participates in the implementation of insulin biological functions, normalizing fat metabolism, hematopoiesis, as well as necessary for normal functioning of the hypophysis and pancreas.

The purpose of research is to obtain and investigate the composition of malts with high content of deficient micronutrients and enrichment with selected raw materials the rye-wheat bread.

Materials and methods

Materials

The subject of research is malt of cereals (maize and oat), salts of chromium and zinc, mineralized grain crop's malt, rye-wheat bread enriched with the composition of mineralized malts.

Methods

To obtain mineralized grain raw materials, maize and oat were germinated using solutions of zinc salt (ZnSO4) and chromium one ($CrK(SO_4)_2 \times 10H_2O$). Germination was carried out at a temperature of 17-18 °C. When required humidity of the grain (47%) reached, the soaking solution with salts was drained and the grain was left for germination, stirring and moistening it periodically with the same mineralized solutions.

In the process of raw materials, semi-finished products and finished product research there are used titrimetric, photocolorimetric, refractometric and sensory evaluation conventional methods of research [27]. X-ray fluorescence analysis was used to determine the mineral composition of grain and malt [28, 29] and stripping voltammetry method [27, 30] to determine the zinc content.

Results and discussion

Obtaining and researching the composition of mineralized malts

Current trends in consumption of products with reduced caloricity and increased nutritional value require innovative solutions in the process of creating a new range of bakery products. Vegetable raw materials with high nutritional and biological value include germinated grain products. The sprouted grain (malt) contains the entire set of ingredients needed for efficient nutrition: essential amino acids, carbohydrates (sugars, dextrins, dietary fiber), minerals, vitamins, dyes and polyphenolic compounds. The production of malt flour involves grain soaking, germination and drying.

To determine the zinc ions effect on the process of maltening of maize and oat grains there were used zinc sulfate solutions of different concentrations: 0.001, 0.002, 0.003, 0.004 and 0.005%.

The results of studies of the zinc ions effect on the intensity of maize and oats germination are shown in Figure 1 and Figure 2 respectively.

The data shows that germination energy 13–14% higher for oat and maize grains at 0.002% zinc salt concentration in comparison with pure water.

Zinc content of maize and maize malt was investigated by inversion voltammetry [27, 30]. With the chosen optimum concentration of 0.002% zinc salt in soaking water, it was determined that the zinc content of the enriched maize increased by 6.7 times compared to the original grain (Table 1). The zinc content of the grain does not exceed the maximum permissible concentration of 50 mg/kg.

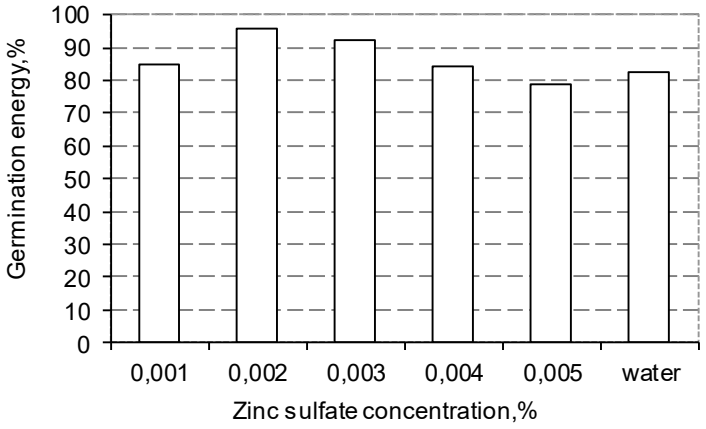

Figure 1. Investigation of zinc ions influence on the process of maize grain germination

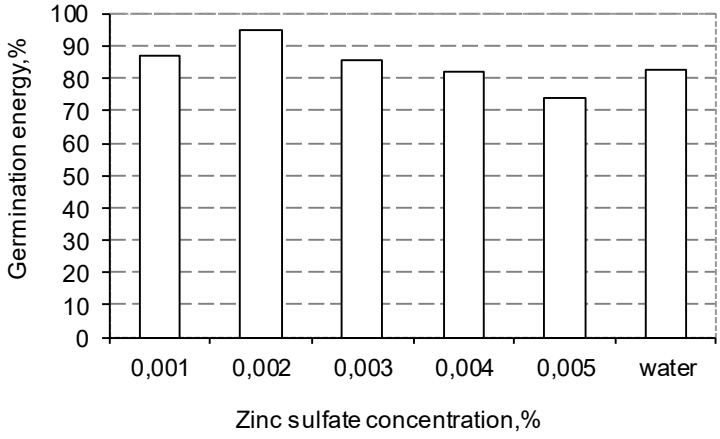

Figure 2. Investigation of zinc ions influence on the process of oat grain germination

Table 1

Investigation of zinc accumulation in maize

Name of the mineral	Mineral content, mg/kg	
	In the source grain	In the enriched grain
Zinc	1.7	11.4

The germination of oat and maize grains was studied using different concentrations of the chromium salt solutions $CrK(SO_4)_2 \cdot 10H_2O$ (Figure 3 and Figure 4).

The figures show that the 0.001%chromium salt concentration in the soaking water leads to an increase of the grain germination energy at 12–13 % compared with the intensity of germination in water. With increasing concentrations of chromium salt in soaking water (0.002–0.004%), the germination energy of maize and oat grains decreases. Therefore, for the enrichment of grain with chromium ions, the concentration of chromium salt in soaking water should not exceed 0.001%.

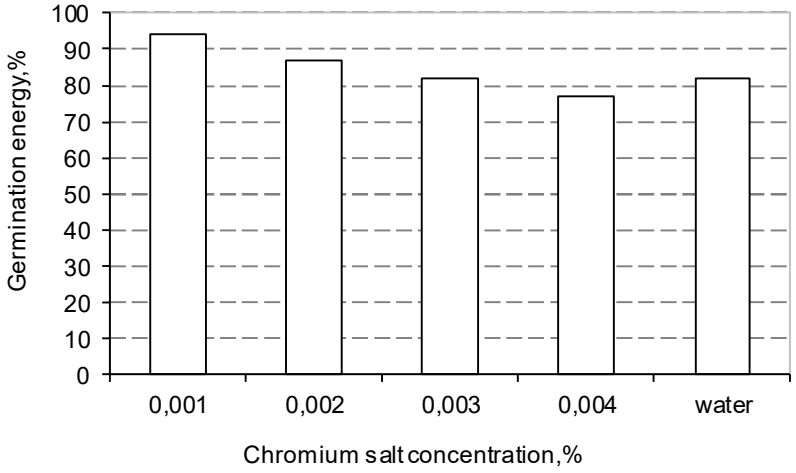

Figure 3. Investigation of chromium ions influence on the process of oat grain germination

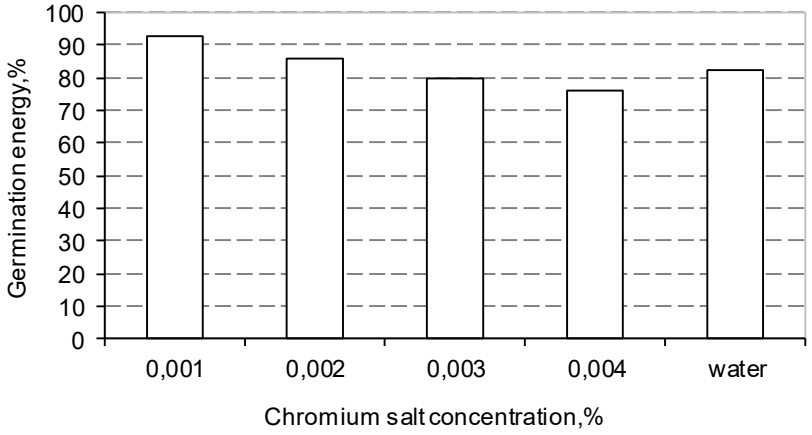

Figure 4. Investigation of chromium ions influence on the process of maize grain germination

X-ray fluorescence analysis was used to study the mineral composition of oat grains and malt [28, 29, 3130]. According to the X-ray fluorescence characteristics of oat grain, oat malt and mineralized oat malt [31], the results of the mineral accumulation study are given in Table 2.

From the analysis of results, it follows that the mineral content is increasing, the content of zinc in enriched malt increased by 6 times in comparison with the original, and that of chromium by 3 times.

Thus, the conducted studies indicate the possibility of the source raw material mineral composition correcting by soaking and germinating grain in aqueous solutions of microelement salts. The addition of such mineralized raw materials to food products formula will enrich them with biologically active substances, giving them functional properties.

The sensory and physicochemical parameters of the obtained mineralized malt were determined. According to the results, the obtained malts are in accordance with all indicators of the normative documents.

Table 2

Mineral content in oat grains and malt when enriched with zinc and chromium salts

Element	Oatgrain	Oatmalt	Mineralized with zinc oat malt	Mineralized with chromium oat malt
	Massconcentration, mg/kg			
Zn	1.87	2.07	11.72	2.18
Cr	0.19	0.71	0.67	2.25
K	113.67	144.55	148.32	135.12
Ca	56.60	60.49	66.40	59.72
Mn	1.31	1.75	1.64	1.58
Fe	2.27	2.49	2.55	2.48
Cu	0.67	0.67	1.10	0.82
S	374.15	497.30	430.33	490.35
Cl	69.59	97.34	109.50	129.46

Enrichment with composition of mineralized malt of rye-wheat bread

To enrich the food with mineralized malts, rye-wheat bread was chosen as the traditional product in this work. Bread is a food product made from flour of different grades with or without baker's yeast. Baker's yeast is adapted to live and grow in a water-flour environment. The bringing into the recipe of bread components that can adversely affect their vital activity is negatively affected on the technological process and quality of the finished product.

So far as selected minerals are active participants of biochemical processes in biological objects and they are active sites of enzymes, it was studied their effect on the activity of the fermentation microorganisms. The developed composition of the mineralized oat and maize malts (malts with a ratio of 1:1) in an amount of 5% there are used. The optimal determined concentrations of zinc salts (0.002%) and chromium salts (0.001%) were used for mineralization. Control was sample with oat and maize malt composition without mineralization.

Experiments (Figure 5) show that mineralized malts have a positive effect on the lifting power of yeast, and more so when zinc salts are added.

This is obviously due to the positive role of the studied metal ions in the activation of yeast cell enzymes, the accelerated synthesis of the cellular enzyme α-glucosidase, which causes the decomposition of maltose to glucose, which is rapidly fermented by the yeast cell, and activates other enzymes of cytoplasm. Alcohol fermentation is intensified as a result of enzyme activation [32].

A positive effect of the mineralized malt flour fraction from maize and oat, enriched (malts with a ratio of 1:1) with zinc and chromium sulfates, on the lifting power of yeast was also found (Figure 6, 7). Apparently, when proportion of malt flour increased the balls floating time is reduced as compared with the control. This indicates a reduction in the duration of the technological process.

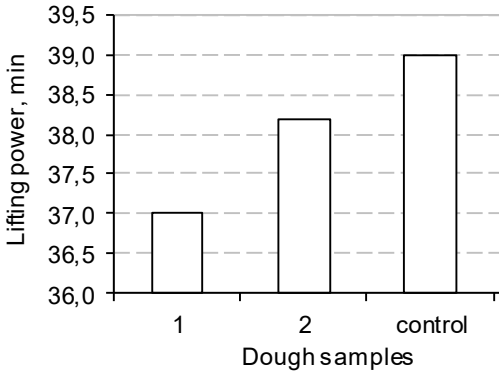

Figure 5. Dependence of baker's yeast lifting power on the addition of malt composition with zinc and chromium salts

1 – test sample with the addition of a malt composition with a zinc salt in soaking water concentration of 0.002%;
2 – test sample with the addition of a malt composition with a chromium salt in soaking water concentration of 0.001%;
Control – is a test sample with the addition of a malt composition without the use of salts.

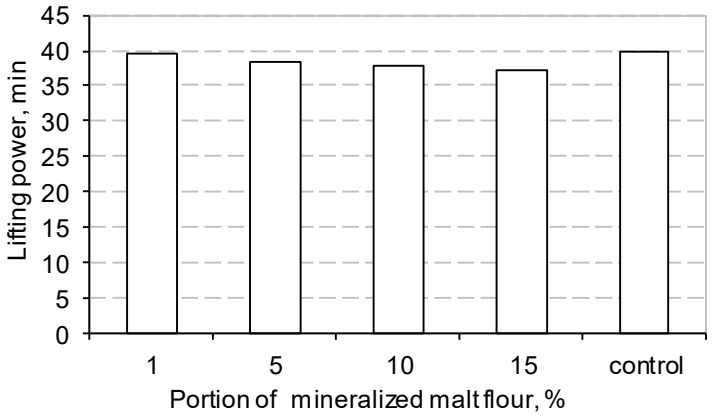

Figure 6. Determination the influence of the composition of malted maize flour with a zinc salt concentration of 0.002% on the yeast lifting power

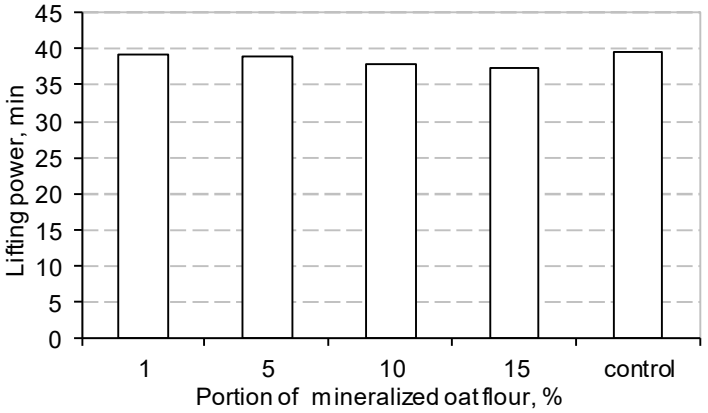

Figure 7. Determination the influence of the composition of malted oat flour with a chromium salt concentration of 0.001% on the yeast lifting power

The experiments of the bread samples baking were carried out to determine the optimal application dose of obtained mineral malts. Determined sensory and physico-chemical indicators of rye-wheat bread with the addition of 5%, 10% and 15% mineralized mixture of malts from oat grains and maize. The results are shown in the Table 3.

Studies of influence of the inserted mineralized malt's weight part on the quality indicators of rye-wheat bread showed that the optimal amount is the introduction of 10% by weight of flour, for which bread with satisfactory sensory and physico-chemical parameters is obtained.

The conceptual technological scheme of enriched bread with the stage of making the mixture of malt at the preparation of the ferment phase is developed. This will reduce the duration of fermentation and increase the biological value of the finished product.

The calculation method [33, 34, 35, 36] determined the content of macro- and micronutrients in rye-wheat bread before and after the introduction of mineralized malt in the amount of 10% by flour weight. It is found that enriched bread increases the protein content by 21%, it is possible to increase the content of such essential deficient amino acids as lysine and methionine, and accordingly improve the utilization coefficient, which shows the level of protein absorption of the product.Thus, the utilization coefficient was 63.8% in the enriched product and 59% in the base product.That is, by adding of selected enrichment protein digestibility increased, with the coefficient of excess amino acid composition, which characterizes the mass fraction of indispensable amino acids and used in the body irrationally, decreased to 12.5%. The goal of the micronutrients content increasing in the enriched finished product, including the microelements Zn and Cr by 2.4 and 1.8 times respectively, was also achieved.

Table 3

Sensory and physico-chemical indicators of rye-wheat bread with the addition of mineralized mixture of malts from oats grain and maize (malts with a ratio of 1:1)

Indicators	Control (rye-wheatbread)	Rye-wheat bread with 5% mixture of malts	Rye-wheat bread with 10% mixture of malts	Rye-wheat bread with 15% mixture of malts
Sensoryindicators				
Appearance: Form Surface	Proper shape, without tears or cracks	Proper shape, without tears or cracks	Proper shape, without tears or cracks	Proper shape, there are small cracks in the crust
Crumbcolor	Brown	Brown	Brown	Brown
Crumbcondition	Baked, with no trace of undermixing; homogeneous, with well-developed porosity	Homogeneous, with well-developed porosity	Homogeneous, with well-developed porosity	Homogeneous, poorly developed porosity, slightly compacted
Tasteandsmell	Inherent to this type of products, without any foreign taste	Inherent to this type of products, without any foreign taste	Inherent to this type of products	Inherent to this type of products, with a noticeable taste of malt
Physico-chemicalindicators				
Specificvolume, cm3/ g	1.92	1.87	1.83	1.77
Humidity, %	45.4	45.5	45.6	46.0
Acidity, deg	6.4	6.5	6.6	6.7
Porosity, %	67	65	64	62

Conclusions

As a result of grain germination, the content of biologically active substances is increased. The germination of grain in a mineralized environment also contributes to the accumulation of minerals in it. Studies have shown that the use of mineralized malt composition in bread technology is expedient, since it contributes to a significant improvement in the content of physiologically active ingredients which provide the health properties of bread.

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Perspective the use of goat milk in the production of soft milk cheeses

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Abstract

Introduction. The purpose of research is analysis the chemical composition, nutritional value and technological properties of goat milk as a potentially promising raw material for the production of soft cheeses.

Materials and methods. Object of research – full-cream goat's milk as raw material in production of rennet soft cheese.

Results and discussion. Biochemical and technological properties of the unique qualities of goat milk are just barely known and little exploited, especially not the high levels in goat milk of short and medium chain fatty acids, which have recognized medical values for many disorders and diseases of people. The new concept of tailor making foods to better fit human needs has not been applied to goat milk and its products so far.

One of the promising areas is the production of soft cheese. Today, soft cheese technologies have been developed to use increased amounts of bacterial preparations and rennet; addition of organic acid solutions, ultrasonic treatment of milk or its concentration by ultrafiltration. By the number of developments that implement the principles of food combinatorics, priority is given to the production of combined products in which raw materials of animal origin are combined with plant components.

In the technology of soft cheeses used vegetable crops in the form of dried powders, legume products, extruded flour from the embryos of chickpea seeds, amaranth flour.

The potential for the development of goat milk-based soft cheeses production corresponds to two trends – product value due to the usage of biologically valuable raw materials and resource-saving and have the increase direction of industrial volumes of goat milk processing and the development of new technologies.

Conclusions. Usage of spices will improve and diversify the taste and aromatic properties of goat milk cheeses, enrich them with a complex of biologically active substances, increase the yield of products and increase their stability during storage.

Introduction

In recent years, more and more people in the world pay great attention to healthy and balanced products made using exclusively natural ingredients. There is a steady increase in demand for farm products that are successfully gaining consumer trust and confidence. Most work on projects for the sale of natural local products.

Moreover, today the cheese market mainly consists of hard cheese, the share of which production structure was some 90%. Pickled and soft cheeses produce in approximately equal amounts, their share in the overall structure is approximately 3% [1].

Therefore, the development of new and improvement of existing technologies for protein dairy products will allow improving food patterns of the population, compensating for the lack of native protein in the diet, increasing the competitiveness of domestic enterprises and taking its appropriate place in both the domestic and foreign cheese markets.

Soft rennet cheeses deserve special attention in the assortment of enterprises. They are a source of digestible native milk protein and have more attractive price policy as compared to hard rennet cheeses.

Historically, up until recently, only private households were involved in goat farming. Today there is a tendency for the development of farmings and small family farms involved in the processing of goat milk [2].

Goat milk and its products of yoghurt, cheese and powder have three-fold significance in human nutrition: 1 – feeding more starving and malnourished people in the developing world than from cow milk; 2 – treating people afflicted with cow milk allergies and gastro-intestinal disorders, which is a significant segment in many populations of developed countries; and 3 – filling the gastronomic needs of connoisseur consumers, which is a growing market share in many developed countries. Concerning 1, very much improvement in milk yield and lactation length of dairy goats, especially in developing countries must be accomplished through better education/extension, feeding and genetics. Concerning 2, little unbiased medical research to provide evidence and promotional facts has been conducted, but is very much needed to reduce discrimination against goats and substantiate the many anecdotal experiences about the medical benefits from goat milk consumption, which abound in trade publications and the popular press. Goats have many unique differences in anatomy, physiology and product biochemistry from sheep and cattle, which supports the contention of many unique qualities of dairy goat products for human nutrition. Concerning 3, a few countries like France have pioneered a very well-organized industry of goat milk production, processing, marketing, promotion and research, which has created a strong consumer clientele like in no other country, but deserves very much to be copied for the general benefit to human nutrition and goat milkproducers. The physiological and biochemical facts of the unique qualities of goat milk are just barely known and little exploited, especially not the high levels in goat milk of short and medium chain fatty acids, which have recognized medical values for many disorders and diseases of people. The new concept of tailor making foods to better fit human needs has not been applied to goat milk and its products so far, otherwise the enrichment of short and medium chain fatty acids in goat butter, and their greater concentration compared to cow butter, could have become a valued consumer item. Also revisions to human dietary recommendations towards admitting the health benefits of some essential fats supports the idea of promoting goat butter. While goat yoghurt, goat cheeses and goat milk powder are widely appreciated around the world, goatbutter is not produced anywhere commercially in significant volume[3].

The potential for the development of goat milk-based soft cheeses production corresponds to two trends – product value due to the usage of biologically valuable raw

materials and resource-saving and have the increase direction of industrial volumes of goat milk processing and the development of new technologies. The advantages of the soft cheese production segment are the economic and technological aspects, which allows the efficient use of dairy raw materials, sale of end product without maturation in order to save labor, energy and financial resources. This is a promising area of scientific research to develop new and improve classical technologies of goat milk based soft cheeses based on the principles of consumer value, resource efficiency and safety.

The **aim** of the research is to study the chemical composition, nutritional value and technological properties of goat milk as a potentially promising raw material for the production of soft cheeses.

To accomplish the aim, the following tasks have been set:

- Justify the choice of raw materials for the production of soft cheese;
- To investigate the chemical composition, nutritional value and technological properties of goat milk as a potentially promising raw material for the production of soft cheeses;
- Justify the feasibility of using natural spices in the production of soft cheeses.

Materials and methods

Object of research – full-cream goat's milk as raw material in production of rennet soft cheese [1, 3].

Scientific and research works, articles, proceedings of the conferences, thesis of the conferences, monographs of different methods, modes, processes of liquid systems treatment and equipment for processing were analyzed.

Results and discussion

Characteristics of the chemical composition of goat's milk

Goat milk is a valuable raw material of high nutritional value, is a source of high-grade milk protein and fat with a high level of digestibility and a number of other nutritional and biologically active compounds [4]. Additionally, to its nutritional value, it is hypoallergenic and exhibits immunological properties [3].

The most valuable component of goat milk is protein, which average content is 3.6% [5] (in cow's milk – 3.2% [5]), and which is presented in highly dispersed state, the average particle diameter of casein micelles is 73 nm [5] (100 nm in cow's milk). It leads to a better digestibility indicator compared to cow's milk protein and is 97% [5].

Protein in general and milk plays a significant role in the normal development and functioning of the human body [1]. It is a source of indispensable amino acids, a structural and functional basis for the formation of nerve, muscle tissue, connective tissues, joints, and human internal organs [1]. It is also a part of all body cells, found in enzymes, hormones, and immune bodies [6].

Furthermore, the protein is the most technologically crucial milk component, the content and characteristics of which depend on the protein dairy products output [6].

It is also worth mentioning that the chemical composition of milk as a whole, including the total protein content, its fractional composition, depends on the goat breed, genotype, season and feeding ration [6].

As an example, a comparative characteristic of the fractional composition of goat (Saanen breed) and cow's milk proteins is given in Table 1.

Table 1

Fractional composition of goat and cow's milk [7]

Protein and its fractions	Goat milk n=80		Cow milk, n=123	
	g/100 ml	%	g/100 ml	%
General protein	**3,196±0,040**	**100**	3,360±0,040**	100
Casein:	**2,452±0,037**	**76,7**	2,609±0,045**	77,6
αs_1	**0,393±0,010**	**16,4**	0,859±0,025***	25,5
αs_2	**0,526±0,027****	**11,5**	0,321±0,009	9,6
β	**1,122±0,014*****	**35,1**	0,767±0,021	22,8
Whey protein:	**0,744±0,001**	**23,6**	0,751±0,012	22,4

The difference in the composition and structure of goat and cow milk proteins is the basis of their structural and physicochemical characteristics. Therefore, a low content of αs1-casein and a higher content of whey proteins, unlike cow's milk, contributes to the softer clot formation, small size and small loose flakes, which facilitates milk digestion by proteolytic enzymes [8]. In this regard, goat milk is easier to digest, does not cause digestive disorders, and has hypoallergenic characteristics [9].

The quantitative content of the αs1 casein fraction has a significant effect on the technological characteristics of milk, in particular cheese quality. Dairy raw materials with higher casein αs1-fraction content are of greater importance in the cheese production, reducing the loss of protein in milk whey when cultivating a clot formed under the action of milk-clotting enzymes [10].

The protein of goat milk is more biologically complete in comparison with the protein of cow's milk. Comparative characteristics of the biological value of goat and cow milk are given in Table 2.

Table 2

Comparative characteristics of the biological value of goat's and cow's milk [10]

The name of the essential amino acid	Content of amino acids, g/100 g of protein		Scale FAO/WHO, g/100 g of protein	Amino-acid score, %	
	Goat's milk	Cow's milk		Goat's milk	Cow's milk
Valine	5,4	5,8	5,0	108,0	116,0
Isoleucine	4,9	5,2	4,0	122,5	130,0
Leucine	7,2	7,6	7,0	102,9	108,6
Lysin	5,7	6,1	5,5	103,6	110,9
Methionine +cysteine	3,7	3,6	3,5	105,7	102,8
Phenylalanine +tyrosine	8,0	7,6	6,0	133,3	126,7
Threonine	4,0	3,6	4,0	100,0	90,0

Based on the analysis of the data in Table 2, we can draw a conclusion about the usefulness of protein in goat and cow milk. The limiting amino acid for cow's milk is threonine, while for goat's milk the score of this amino acid is 100%.

The share of dominant acids of isoleucine and phenylalanine in goat milk protein is quite high and even exceeds the level recommended by the FAO/WHO by 22.5 and 33.3%, respectively. The remaining amino acids exceed the recommended level by 2-8%.

Milk fat is one of the indicators that determines the technological, nutritional quality and biological value. It averages 4.3% [11] for goat milk and 3.6% [11] for cow milk. Fat is present in milk as fat globules. The core of the fat globules consists mainly of triglycerides and is surrounded by a complex membrane synthesized from mammary epithelial cells. A specific feature of the fat composition of goat milk is the small size of globules – an average of 2 microns [11], which is about 10 times less than cow's fat globules. As a result, fat represents a thin fat emulsion that characterizes its homogeneity, does not form foam and aggregates, unlike cow's milk. The small size of the fat globules is safer because of greater absorption of goat milk fat due to the accessibility of the effect of pancreatic lipase [12].

The fatty acid composition of goat milk is mainly represented by short- and medium-chain fatty acids (C6:0-C14:0) – caproic acid, caprylic acid, caprinic acid and lauric acid [13]. Short and medium-chain triglycerides, as an energy substrate for enterocytes, improve nutrient transportation through the cell membrane and contribute to the restoration of damaged cells of the intestinal mucosa [14].

Goat milk contains 2 times more low-molecular weight fatty acids, as compared with cow milk, which determines the specific taste and after-taste of goat milk, especially taking into account the content of caproic, caprylic and caprinic acids [14].

Despite the increased content of low molecular weight fat, the stability of goat milk fat stage to thermal and enzymatic factors of influence during production has been proved [12].

Quality, processing ability and sensory properties of milk are highly correlated with content and composition of milk fat. Biologically active lipid substances are primarily saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs; linoleic acid; C18:2 n-6) and polyunsaturated fatty acids (PUFAs; α-linolenic acid; C18:3 n-3). PUFAs with 20C, mainly docosahexaenoic acid (DHA; C20:5 n-3) and eicosapentaenoic acid (EPA; SC22:6 n-3), are precursors of eicosanoids, which regulate various physiological processes. Fatty acid composition depends on many different factors, such as animal species, breed, season, lactation stage, geographical location, and diet. Goat and sheep milk are rich in the medium chain fatty acids, caproic (C6:0), caprylic (C8:0) and capric (C10:0), which is the reason for the specific aroma of those kinds of milk. Goat and sheep milk have more conjugated linoleic acid, and usually lower n-6/n-3 ratios, with higher amounts of α-linolenic acid, compared to cow milk. Compared to goat and cow milk, sheep milk has the lowest amounts of lauric (C12:0), myristic (C14:0) and palmitic (C16:0) acids i.e. fatty acids associated with negative effects on human health. The addition of forage, especially fresh grass, to dairy animal diets enhances the proportion of unsaturated fatty acids in milk fat compared to SFAs and increases the amount of conjugated linoleic acid [15].

Goat milk is globally consumed but nutritional profiling at retail level is scarce. This study compared the nutrient composition of retail cow and goat milk (basic solids, fatty acids, minerals, and phytoestrogens) throughout the year and quantified the potential implications on the consumers' nutrient intakes. When compared to cow milk, goat milk demonstrated nutritionally desirable traits, such as lower concentrations of C12:0, C14:0, C16:0 and Na: K ratio, and the higher concentrations of cis polyunsaturated fatty acids (PUFA), eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), isoflavones, B, Cu, Mg, Mn, P and I, although the latter may be less desirable in cases of high milk intakes.

However, in contrast with nutritional targets, it had lower concentrations of omega-3 PUFA, vaccenic acid, lignans, Ca, S and Zn. The extent of these differences was strongly influenced by season and may demonstrate a combination of differences on intrinsic species metabolism, and farm breeding/husbandry practices [16].

One of the important characteristics of both dairy raw materials and final products is availability of minerals and vitamins. Both goat and cow milk are characterized by a high degree of mineralization. Goat milk has a high potassium content, which plays an important role in the activity of the cardiovascular system. Goat milk has a high content of calcium, copper, vitamin C, D, A, B and PP. Goat milk, in comparison with cow milk, has a lower iron content, however, the degree of its assimilation is higher (30%) as compared to the cow milk (10%) [17, 18].

Goat milk contains a significant level of carbohydrates (4.6% averagely), namely a class of oligosaccharides that have prebiotic characteristics, thereby promoting the growth of bifidobacteria in the gastrointestinal tract. With the proper microflora of gastric colonization of bacteria, complex carbohydrates, as well as lactose, are broken down into several components of monosaccharides, which are then metabolized to side-products, with subsequent transformation into an energy source [19, 20].

Milk oligosaccharides are compounds capable of modulating intestinal microbiota by exerting a prebiotic, anti-adhesive and anti-inflammatory effect. Technological advances in equipment and analytical methods have indicated that goat milk is a good source of oligosaccharides, and that some of these oligosaccharides are similar to those found in human milk. Scope and approach: This review focuses on recent scientific information regarding the structure and composition of oligosaccharides in goat milk and their benefits, thereby providing an overview of what has been tested and proven about goat milk. Key findings and Conclusions: The quantification and the profile of oligosaccharides depend on the methodology applied for this purpose. Those based on HPLC and mass spectrometry are the best methods for oligosaccharide identification and quantification in goat milk. Membrane technology is also a successful method applied in the isolation and concentration of oligosaccharides. Beneficial effects of goat milk oligosaccharides are related to gastrointestinal activities, inflammatory reactions and nervous system development [21].

Analysis of the current state of technology of soft cheese

One of the promising directions is the soft cheeses production. However, the difficulty is both the lack of raw materials and technological features due to the low titratable acidity, the fractional composition of the protein (dominance of β-casein, and α-lactalbumin) and slower coagulation under the action of rennet.

The technology of goat milk soft cheeses production has been developed with the usage of high doses of bacterial starter cultures and calcium chloride, due to which the rate of clot syneresis and cheesecurd dehydration has been increased [18].

In order to increase the density of a goat milk clot, it was proposed to launch a method for preparing goat milk by increasing its titratable acidity to 21°T by introducing aqueous solutions of organic (citric, ascorbic) acids and their mixture in an amount of 0.01-0.04 wt.%. This made it possible to increase the density of rennet clots, reduce the loss of milk proteins with cheese dust and provide an increase in rennet cheese withdrawal from 1 ton of goat milk by 1-2% [19].

Among the developments in which the principles of food combinatorics are implemented, the priority belongs to the production of combined products in which raw materials of animal origin are combined with plant components. Both cereals, for example,

wheat, rice, oats, and legumes such as soy, chickpeas, lentils, and the like are widely used in the capacity of vegetable raw materials used in the production of combined foods.

In products with complex composition milk and vegetable raw materials are used in different combinations, which allow to give them certain functional properties. Increasing the production of biologically wholesome products is a highly topical issue. One of the possible solutions of the problem is combining milk basis with vegetable raw material. Studies have been conducted on the development of soft cheeses from goat's milkwith chickpea flour. The aim of this research is to study the properties, consumer value and possibility of creation of soft cheese formulation with chickpea flour. In this field of study, an extruded chickpea flour is an innovative additive that had never been used before. Optimal proportion of ingredients was determined by nutritional, biological and energy value under the limitations arising from structural and parametrical models of adequate nutrition. The optimal concentration of bean filler in cheese mass that allows for the insignificant change in qualitative indicators of lacto-vegetarian product (taste, smell, consistency and color) was determined. During the experiments an effective fracture of bean component was selected and qualitative indicators of the developed soft cheese were determined. The paper gives scientific substantiation for the effectiveness of manufacture of soft goat cheese with chickpea flour [22].

Technological techniques such as bioactivation of cereals and legumes, including those with the simultaneous enrichment of essential microelements (iodine, selenium) and extrusion [23-25], have positively established themselves as pretreatment of leguminous crops.

In the technology of soft cheeses and cheese products, vegetable crops are used in form of dry powders, for example, girasol, and sterilized mashed puree for example, from carrot [26].

The technology of goat milk soft cheese has been developed. The implementation of this technology uses legume processing products – lentil and chickpea flour as functional additives, applied with the aim of saving resources. The definitive weight content of bean filler for lentil flour is 3%, for chickpea flour – 5% by weight of the product [27]. It has been established that the use of the bean component affects the change in the acidity of the product and contributes to an increase in the product yield by 2.5% on average [27].The disadvantage is that the flour of legumes is an additional favorable environment for the development of extraneous microflora, which leads to a reduction in expiration dating period.

A technology of introducing spicy aromatic and medicinal herbs to goat milk has been developed in order to improve its technological features. A well-known method for the production of soft cheese without ripening, in the implementation of which the functional phytocomponents of medicinal plants (0.5-1.5% by weight of the initial mixture) and soluble dietary fiber (0.3-0.5% by weight of the initial mixture) are intended to be applied in a dry, finely divided form into the mixture before formation (after removal of up to 70% of serum) [28].

Food fibers, which are introduced in an amount of 0.3-0.5%, can increase the final product yield by 5-7%. They also contribute to the extension of expiration dating period, preservation of freshness and improvement of organoleptic characteristics of cheese [28].

A special research was conducted in which extruded flour from chickpea seed embryos and dry powder of crushed girasol fibers were selected as plant components. A feature of obtaining chickpea embryos is the introduction of selenite and potassium iodide into the nutrient medium during germination, due to which they are organized and bioavailable. Food fibers in the composition of plant ingredients expand the range of functional properties of goat milk, and in combination with probiotic cultures, they provide the symbiotic properties

of the final product. Improving the technology in this manner is appropriate, since food fibers are hydrocolloids and have the ability to bind and retain moisture, that increases of product yield [29].

The technology of soft cheese with Amaranth powder has been also developed. Amaranth powder is intended to be introduced into pasteurized and cooled to a temperature of 28-32°C milk in an amount of up to 7.5% by weight of the mixture. Amaranth flour was prepared at a temperature of 120 ... 130° C. The resulting mixture was thoroughly mixed for 10-15 minutes. Further, the technological process was carried out according to classical technology. The use of amaranth flour provides an increase in the nutritional and biological value of cheeses, enriches micro- and macroelements, facilitates to save raw material resources and to reduce the cost of the final product [30].

However the demand for goat milk products remains persistently high, the lack of raw materials limits the volume and range of such products and causes a higher cost. Additionally, the perceptual aspect of goat milk products, such as a more intense smell and taste, also contribute to the low perception of these products by some consumers. In this context, the partial replacement of goat milk with cow milk as part of a product such as cheese may be an alternative for consumers who want to consume more dairy products from goat milk. Partial replacement of goat milk with cow milk may provide an opportunity to diversify the dairy market, since it allows creating products with high nutritional value and unique characteristics compared to products made exclusively from cows milk [31].

In the domestic market of Brazil one of the traditional and widespread is fresh cheese Minas [32]. Advantages in the production of Minas cheese are a short technological cycle, high final product yield and high consumer properties.

Fresh cheese Minas is produced in the result of enzymatic coagulation of goat, cow and a mixture of goat (50%) and cow (50%) milk from starter cultures (R-704 *Lactococcuslactis*ssp *Lactis* та *Lactococcuslactis* ssp *Cremoris*; ChrHansenIndústria e Comércio Ltda, Valinhos, Brazil) or with subsequent processing of the clot, self-pressing and salting in brine. It has a soft texture, slightly acidic aroma and high moisture content. Cheeses were vacuum packed in sterile plastic bags and stored for 21 days at 4°C. It was determined that all control samples showed similar physicochemical characteristics and storage ability, except hardness – cheese based on goat milk had a very soft structure and higher moisture content. Although, the goat milk-based sample had a specific taste and smell, which is due to the higher content of caprylic, caprinic, oleic and linoleic fatty acids in comparison with cheese made from cow milk. The color of such cheese is white with a less noticeable yellowish tint, typical for cheeses based on cow milk. Therefore, the development of derivative products, in particular fresh Minas cheese with partial replacement of goat milk with cow milk, can be a viable alternative to marketable, high-quality dairy products that meet demand of a wider range of consumers [32].

A similar technology was developed for Coalho cheese using a mixture of cow and goat milk to obtain a product with the appropriate physicochemical, organoleptic characteristics and satisfactory consumer perception.Cheese samples based on cow, goat and a mixture of cow and goat milk were made according to the traditional technology for Coalho cheese, suggested by the Brazilian research company Embrapa. A particularity of this technology is the heat treatment of cow milk, goat milk or a mixture of cow and goat milk (1:1) at 90 ± 1°C by aging in containers for 10 minutes and subsequent acidification with lactic acid in an amount of 0.25 ml/l.Milk (its mixture) was refrigerated to a temperature of (36 ± 2)°C, then the technological process was implemented according to the classical technology for soft cheeses with rennet-acid coagulation of proteins [33].

Studied that thermosonication was used as a combined treatment of raw goat milk (RGM) using pasteurization (72 °C for 15 s) and ultrasound treatments (20 kHz at the power variance of 150 W, 200 W, 300 W and 400 W for 10 min). Investigation on the impact of the microbial load, protein content, protein aggregation, the particle size of fat and casein micelles, pH, viscosity, turbidity, color, and soluble calcium and phosphorus contents were carried out, whiles RGM and PGM served as the control. Our results revealed that at 400 W, that thermosonication resulted in a significant reduction ($\alpha = 0.05$) in the microbial load of the samples to less than 2.3 log cfu/mL in comparison to those of RGM and pasteurized goat milk(PGM) at 5.94 log cfu/mL and 4.76 log cfu/mL respectively. In RGM, the fat size (3.5 μm) decreased to 0.4 μm at 300 W; while those of casein micelles also decreased from 406 to 256.4 nm at 400 W. However, no significant effect was observed in the color and soluble calcium and phosphorus contents of all samples. The effect on the microbial load and fat homogenization would promote thermosonication process in the dairy industry [34].

As an alternative to pasteurization and in order to improve the coagulation properties of milk under the action of rennet the studies on the effect of ultrasonic pretreatment on goat milk before coagulation are being conducted [35].It is common knowledge thatpart of milk proteins, in particular whey proteins, are thermolabile and at temperature processing above 60°C they are denatured and partially coagulated.The use of ultrasound is suggested as an alternative to pasteurization. It does not lead to coagulation of non-thermostatic milk proteins. The studied milk was subjected to ultrasound at 800W for various amounts of time (0-20 sec). It is established that compared with the control sample, which was not amenable to ultrasonic treatment, the degree of protein denaturation of the studied samples increased by 9.57%, the content of soluble calcium and phosphorus by 16.9 and 13.7%, respectively. Clot density, coagulation rate water-holding ability and expiration dating period of produced products also increased.

One of the promising methods for processing dairy raw materials in the production of soft cheeses is ultrafiltration.It helps to improve traditional and develop new technological approaches, while minimizing the denaturing effect on proteins, vitamins and other biologically active components of raw materials [36].

The ultrafiltration method allows one to obtain a concentrated mixture and save 20-25% on the consumption of electricity, steam, and starter samples Ultrafiltration processing of milk allows to increase the yield of fresh cheeses by 20% and reduce the cost of rennet by 30% [37].

The manufacturing procedures and compositional characteristics were studied for fresh soft cottage cheese (Domiati type) made from goat milk using ultrafiltration (UV) and without its use [38].It was determined that cheeses obtained with a concentrated mixture had a lower pH, moisture and ash content, while protein and fat were higher in comparison with cheeses made from whole milk.The use of milk ultrafiltration ensured an increase in cheese yield by 21%, protein utilization by 21 ... 26%, fat 15 ... 19%.Moreover, the ultrafiltration process showed a decrease in the total time for the technological process, and reduced the consumption of salt, starter cultures, milk-clotting enzyme and calcium chloride, respectively, and positively influenced the consistency of cheeses.

Scientists at the Ukrainian State University of Food Technologies suggested using fenugreek and turmeric in production of goat milk soft cheeses. They are a source of biologically active substances and components that ensure the stability of quality indicators of final products during its storage.It was found that adding spices to the normalized mixture before thermal conditioning in the amount of $1.0 \pm 0.2\%$ leads to a decrease in the active acidity of goat milk and serum, allocated during processing of rennet in an average of 0.2 pH

units. Besides, it provides the formation of a denser clot, accelerates serum separation, probably due to the adsorption of components of spices on the surface of casein micelles and, as a result, a decrease in their surface charge and aggregation [39].

Natural spices in protein-based technology

Spices are a source of biologically active compounds (essential oils, terpenoids, phenolic and polyphenolic substances, vitamins, micro- and macronutrients, etc.), that evince antioxidant antimicrobial and bacteriostatic effects [40].The food industry typically uses dried vegetable raw materials containing from 8% to 14% moisture [41].

Natural spices have a high content of aromatic substances, which are mainly essential oil. The amount of aromatic substances in natural spices is subject to considerable fluctuations. Thus, in some plants the content of aromatic substances is up to 1%, while in others it reaches 14% or more. Particularly rich in essential oil of the family of conifers, labia flowers, umbrellas [41].

By forming the taste properties of products, spices also increase the activity of the effect of food on the digestive system, contributing to a better absorption of nutrients. This is not only due to the more intense secretion of gastric juice, but also due to the spice content of the components, which are catalysts for a number of processes and contribute to the intensification of metabolism as a whole [42].

Thus, natural spices are a promising raw material not only for the preparation of culinary dishes, but also can be used as an enrichment component in the composition of dairy products. The use of spices is quite limited. Therefore, at the current level of dairy technology development, the actual task is to use spices in their composition.

Ripened cheese varieties containing herbs are traditional in Turkey and have been manufactured for more than 200 years in the east and southeast of the country. They are manufactured from raw milk, semi-hard in texture and salty in taste and have the aroma of garlic or thyme due to added herbs. Twenty-five types of herb, including Allium, Thymus, Silene and Ferula species which are most popular, are used individually or as appropriate mixtures. The most popular of these cheeses is Otlu which is produced mainly in the Van province of Turkey in small dairies and villages, but now is produced in other cities of the eastern region of Turkey and its popularity increases continuously throughout Turkey. The manufacturing technology, chemical, biochemical and microbiological status of Otlu cheese and the most common herbs used in its manufacture are reviewed. The possible effect of herbs used on the biochemical and microbiological characteristics of the cheeses are discussed also. In addition, some varieties of Otlu cheese and cheeses flavoured with spices(chilli pepper, black pepper, cinnamon, allspice, mint, thyme, cumin, etc.), including Carra, Surk and related cheeses, are discussed briefly [43].

Essential oils (EOs) are natural substances extracted from aromatic and medicinal plants (AMPs), important in food preservation. Several studies have shown that AMPs, as well as their EOs have antimicrobial (antibacterial and antifungal) activity. Indeed, our in vitro studies have shown that oregano and thyme EOs are effective against foodborne bacteria, isolated from fermented meat products and cheeses, such as Escherichia coli, Listeria monocytogenes, Salmonella spp., and Staphylococcus aureus. However, EOs of thyme and oregano seem to control the growth of fungi, namely Botrytis cinerea and Aspergillus spp., affecting the shelf-life of fruits during postharvest. The EOs of sage and rosemary have shown little or no antimicrobial activity. Shelf-life extension studies using several EOs (cinnamon, clove, oregano, rosemary, sage, and thyme) and AMPs were performed using pork meat, goat cheese, strawberries, and table grapes. Preliminary results regarding food

safety and sensory acceptability are discussed. Practical applications Consumers' demands for more traditional and healthier food products led to a search for alternatives to replace synthetic by natural additives. EOs of AMPs contribute to food safety, due to their antimicrobial properties. Consequently, the use of AMPs' EOs may also extend the shelf-life of food products. In the present study, experimental shelf-life trials using EOs with different food products were performed, with promising preliminary results. Cinnamon, sage, and thyme EOs extended the shelf-life of strawberries and table grapes. Oregano EO prolonged the shelf-life of soft cheese. Thyme EO controlled the population of enterobacteria present in pork meat. Furthermore, the conditions used in this study can be directly applied in the food industry. Moreover, AMPs may be interesting alternatives to replace or reduce artificial food additives [44].

Despite the availability of scientific findings and research, the high nutritional value and functionality of goat milk, its industrial processing in our country is only just beginning to be introduced. The technology of soft cheeses requires a search of new ways to improve the organoleptic and functional characteristics, the stability of quality indicators during storage, and increase the level of resource and energy efficiency of production.

Conclusion

1. The limitation for the wider use of goat milk for industrial processing lies in its worse ability to coagulate under the influence of rennet, due to the fractional composition of the protein and low titratable acidity. This requires additional adjustment of the technological characteristics of goat milk, which is currently performed either by mixing with goat and cow milk, or by adding food additives, both natural and synthetic.
2. A promising area of scientific research is to improve the technology of soft goat cheeses by using natural ingredients, in particular spices, to improve and diversify the taste and aroma characteristics of goat milk cheeses, enrich them with a complex of biologically active substances, increase the yield of products and increase their stability during its storage.
3. The collaborative mechanism of milk components and spices requires a theoretical explanation, providing the desired technological effect and original organoleptic characteristics of the products.

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Differentiation of Omani Acacia and white Acacia honey by botanical and physicochemical analysis

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Abstract

Introduction. Consumer in the Middle East market can be confused with two types of Acacia honeys i.e., 'true Acacia' honey from Acacia tortilis and 'White Acacia' honey from Robinia pseudoacacia.

Materials and Methods. In this study, we evaluated honey samples to characterize and differentiated true Acacia from Robinia honey using botanical and physicochemical characteristics. Acetolysed pollen from honey was used to determine pollen concentration to establish the purity and floral origin.

Results and Discussion. Acacia honey showed mean pH 4.83, moisture content 16.75%, EC 1.82 mS/cm, free acidity 95.30 meq/kg, diastase activity 12.00 DN and invertase activity 141.07 U/kg which are on par with the permitted specifications except EC and free acidity, being relatively higher. Robinia honey samples have pH 3.80, moisture content 17.41%, EC 0.33 mS/cm, free acidity 8.03 meq/kg, diastase activity 8.00 DN and invertase activity 17.53 U/kg. These values meet the standards. The EC of Acacia honey correlated with pH, moisture content, free acidity, diastase and invertase activities indicating richness in minerals and organic acids. All parameters were relatively higher in Acacia than in Robinia honey.

Conclusion. We recommend that honey be labelled with specific names. We suggest the name "Acacia" for Acacia spp. honeys and "Robinia" for Robinia pseudacacia honey.

Abbreviations

AOAC – Association of Analytical Communities,
CAC – Codex Alimentarius Commission,
DN – Diastase number,
EC – Electrical conductivity,
EUC – European Union Council,
GSO – Gulf Cooperation Council Standardization Organization,
ICBB – International Commission for Bee Botany,
IHC – International Honey Commission,
mS/cm – milliSiemens per cm,
meq/Kg – Milliequivalents per liter,
U/Kg – Units/kg.

1. Introduction

Oman in Eastern Arabian Peninsula has many agro-climatic regions and diverse flora that provides potential for different types of honeys. Omani honey is well known for its characteristic aroma, taste and texture and has been awarded a gold medal at National honey show in London in 2012 (National honey show, 2012). In Middle East countries, the most popular unifloral honeys are *Acacia* (*Sumr*), *Ziziphus* (*Sidir*) and *Prosopis* (*Ghaf*) honeys (Sajwani et al., 2007). In northern Oman, true *Acacia* honey is produced in summer by bees from *Acacia tortilis* (Forsskal) Hayne., which is the most common wild tree distributed throughout the country (Sajwani et al., 2007 and Sajwani et al., 2014). *Acacia* honey is very famous in this region due to its nutritional and medicinal properties. It is characterized by strong aroma and flavor; has a thick texture and does not crystallize. The color ranges from light amber to dark amber with moderate amount of sugar (Sajwani et al., 2007 and Sajwani et al., 2014). White *Acacia* honey is produced from the nectar of *Robinia pseudoacacia*, which is a typical European honey and studied well (Persano Oddo and Piro, 2004). The consumer can be confused with the name Acacia and White Acacia, so the present study was carried out to evaluate and characterize *Acacia* honey using melissopalynological and physicochemical analysis. Physicochemical parameters have been considered as quality criteria for the characterization of honey types (Lazarević, et al., 2012) that are strictly regulated by legislative standards by IHC, CAC and AOAC (Persano Oddo and Bogdanov, 2004). There are several reports on the use of physical and chemical parameters to characterize honey from different countries (Juszczak, et al., 2009; Khalil, et al., 2010; Saxena, et al., 2010). However, the physicochemical characterization of honey from Arabian countries is not comprehensively determined and more so little information is available on the physicochemical properties of Omani *Acacia* honey. This work aimed to establish values for authentic Omani *Acacia* honey and to determine whether it meets national and international standards of honey and to differentiate it from European *Robinia* honey.

2. Materials and methods

2.1. Honey samples collection

Eighty samples of *Acacia* honey (Ac1 - Ac80) were collected during summer season from nine governorates of Oman (Figure 1). The honeys from *Apis florea* and traditional (*tubl*) combs were collected by pressing them manually, while the honeys from *A. mellifera* frame hives were extracted by centrifugation. Authenticated pure honey samples were obtained directly from honey cells to ensure that the sample was not mixed with pollen stores in the comb. It was made sure that beekeepers did not feed the bees with any external supplement of pollen pellets and the honey samples were not heated and filtered. Fourteen *Robinia* honey samples (Rb1 – Rb14) were purchased from local markets in Muscat that were imported from different European countries and China. All honey samples were subjected to quantitative and qualitative pollen analysis to determine their floral origin.

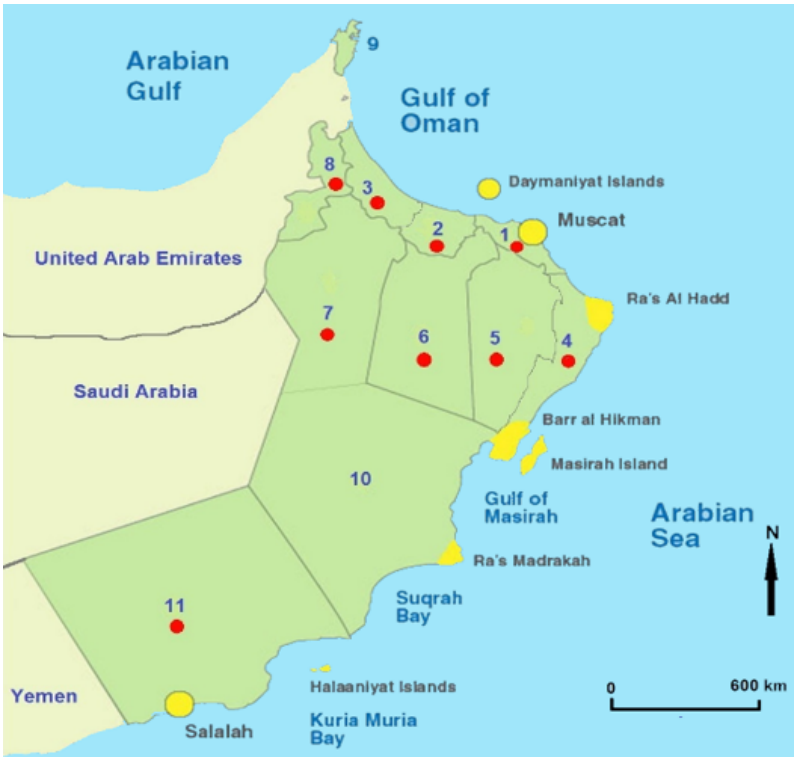

Figure 1. The location of sites (marked with red dots) of sample collection of *Acacia* honey in Sultanate of Oman:
1. Muscat, 2. Al Batinah South, 3. Al Batinah North, 4. Ash Sharqiyah South, 5. Ash Sharqiyah North, 6. Ad Dakhiliyah, 7. Ad Dahirah, 8. Al Buraimi, 9. Musndam. 10 Al Wusta, 11. Dhofar

2.2. Melissopalynological studies

The polyfloral character of honey samples was confirmed according to melissopalynological methods reported by Erdtman, (1960); Nair, (1970); Louveaux et al. (1978) and Jones and Bryant, (2004).

2.2.1. Quantitative analysis. Pollen counts were made from slides prepared from the honey samples following the method recommended by ICBB (Louveaux et al., 1978). For determining the honey type, 300-500 pollen were counted from each sample. Honey with predominant (> 45%) pollen type classified as unifloral honey, while honey with several pollen types in considerable number is classified as multifloral honey. Since Poaceae and Chenopodiaceae pollen are airborne, their numbers were subtracted from the total number of pollen grains prior to calculating the frequency of pollen from nectar-producing plants.

2.2.2. Qualitative analysis: Pollen Concentration Count. The pollen concentration count in a honey can form a basis for determining the floral source, as well as assessing the purity of the product. Addition of a known number of exotic pollen or spores to a known volume of honey sample is often used in determination of the pollen concentration (Maurizio, 1975). In this study, *Lycopodium clavatum* spores (Figure 2A) were used as common markers in absolute pollen analysis. One tablet of *L. clavatum* spores (Lund University, Batch 1031, containing 20,848±1546 spores) was dissolved in 5 ml of 5% hydrochloric acid and added to each 10 g of honey sample following Stockmarr, (1971). Then each sample was processed using acetolysis (Erdtman, 1960). Counts of 200-300 pollen grains including anemophilous plant pollen were made for all samples unless 1,000 *L. clavatum* spores were encountered first. These spores were also counted but their number was kept separate from the pollen count. Pollen concentration values per 10 g of p-nitrophenyl-α-D-glucopyranoside of honey sample were calculated by computing the ratio of marker spores to counted pollen grains using the following formula:

(Number of pollen grains counted X Number of *Lycopodium* spores added)/ Number of *Lycopodium* spores counted) (Maurizio, 1975).

Samples were classified into groups according to the pollen grain content of 10 grams of honey following the scheme of Maurizio, (1975); (Group I: < 20 000; Group II: 20 000–100 000; Group III: 100 000–500 000; Group IV: 500 000–1 000 000; Group V: >1 000 000).

2.3. Physicochemical analysis

Standard physicochemical analytical methods were used for honey classification which are validated and harmonized by the IHC (Bogdanov, 2002) and are within the scope of the CAC honey standards (Codex Alimentarius Commission, 2001), EUC (European Commission, 2002) and GSO (2008). Analysis of each sample was carried out in triplicate for each test.

The pH was measured by a pH meter (Mettler Toledo, USA) in a solution containing 10 g honey in 75 mL of freshly boiled warm, distilled water as per the method 962.19 of AOAC (1990). Moisture content was determined following the method of Codex Alimentarius Commission (2001) using a refractometer (Atago 3840 PAL-22S) and the percentage of moisture was measured at room temperature (25±1°C). Electrical conductivity (EC) of each honey solution with 20% dry matter was determined by a conductivity meter (Accumet Ap85) following protocol of the IHC (Bogdanov, 2002). Free acidity was determined using the titrimetric method of AOAC (1990). The honey solution in distilled

water was titrated to an end point of (pH 8.5) with an alkali solution. The results are expressed in milliequivalents acid per 1000 g (meq/kg).

Diastase activity was determined photometrically by Phadebas method (Bogdanov, 1984). The absorbance of the solution was read at 620 nm. Results of diastase activity were expressed as a diastase number (DN) in Gothe or Schade units per gram of honey (Serrano, Espejo, Villarejo, and Jodral, 2007). To measure the invertase activity Siegenthaler's (1977) method was used. It is based on the spectrophotometric measurement of p-nitrophenol at 400 nm, which is formed by the reaction of honey invertase with p-nitrophenyl-α-D-glucopyranoside (pNPG), used as a substrate. Results were expressed as units/kg (U/kg).

2.4. Statistical analysis

Statistical analysis for calculating the means and the standard deviation of the mean were performed using Microsoft Excel software. All results are expressed as the Mean±Standard Deviation (SD). Furthermore, SPSS 22.0 was used for the evaluation of correlation matrix, one-way ANOVA and t-test, as well as the post hoc Tukey's HSD, at the $P < 0.05$. For representation in the tables, the data of 10 samples each is pooled in this publication.

3. Results and discussion

3. 1. Melissopalynological studies: the floral origin of the honey

Among Omani *Acacia* honey samples, the pollen (Figure 2B) percentage ranged from 45.06% in Ac4 to 96.32% in Ac74 (Table 1). These honey samples were dark amber colored, which is typical of unifloral *Acacia* honey. All the *Robinia* honey samples were unifloral with predominant (> 20%) *Robinia* pollen (Figure 2C). These honeys were light amber colored as usually seen in typical unifloral *Robinia* honey. The pollen percentages in the *Robinia* honeys ranged from 20.41% in Rb2 to 61.44.32% in Rb11 (Table 2).

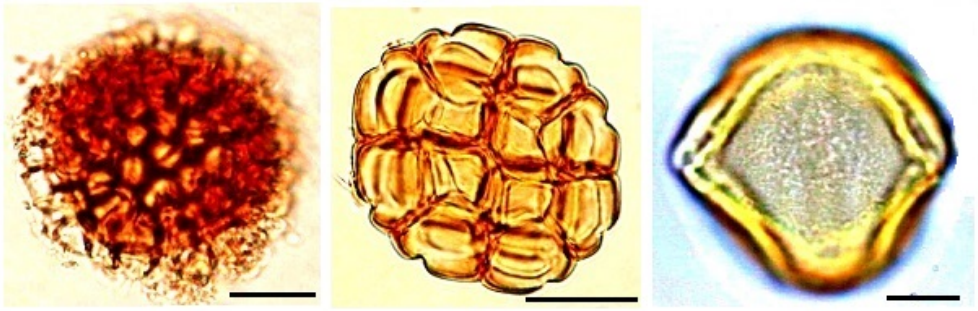

Figure 2. Light micrographs of some significant pollen types and spore recorded in the present study:
(A) *Lycopodium clavatum* (12μm); (B) *Acacia tortilis* (15μm); (C) *Robinia pseudoacacia* (10μm).

Table 1

Pollen and Physicochemical properties of Omani *Acacia* honey samples

No. Of Samples	Pollen (%) Mean	Pollen Conc. Mean	pH Mean±SD	Moisture content (%) Mean±SD
10 (Ac1-Ac10)	58.9	33084.1	4.69±0.07	17.27±0.23
10 (Ac11-Ac20)	56.5	39239.8	4.72±0.08	16.24±0.23
10 (Ac21-Ac30)	61.1	99039.9	4.83±0.04	16.39±0.05
10 (Ac31-Ac40)	69.6	134011.0	4.81±0.03	16.99±0.20
10 (Ac41-Ac50)	64.2	116404.7	4.74±0.03	16.75±0.13
10 (Ac51-Ac60)	67.6	39415.4	4.97±0.04	16.59±0.06
10 (Ac61-Ac70)	67.2	43640.9	5.02±0.03	16.85±0.12
10 (Ac71-Ac80)	67.6	70878.0	4.89±0.05	16.94±0.16
Average of 80 samples	64.1	71964.2	4.83±0.05	16.75±0.15
Min. of 80 samples	45.1	2690.1	4.11±0.04	14.70±0.09
Max. of 80 samples	96.3	499640.1	5.34±0.03	19.20±0.13

Continue of Table 1

No. Of Samples	EC (mS/cm) Mean±SD	Free acidity (meq/kg) Mean±SD	Diastase activity Mean±SD	Invertase activity (U/kg) Mean±SD
10 (Ac1-Ac10)	1.78±0.03	116.96±2.22	14.87±0.33	148.24±0.26
10 (Ac11-Ac20)	1.71±0.02	89.71±4.86	12.31±0.29	144.17±0.49
10 (Ac21-Ac30)	1.86±0.01	88.05±1.27	15.45±0.33	170.20±4.44
10 (Ac31-Ac40)	1.82±0.01	94.94±1.08	9.13±0.26	97.12±2.43
10 (Ac41-Ac50)	1.58±0.02	83.27±0.74	9.30±0.23	107.80±2.48
10 (Ac51-Ac60)	1.83±0.02	88.74±1.43	13.80±0.27	139.81±1.98
10 (Ac61-Ac70)	1.90±0.01	93.01±0.84	10.10±0.29	172.96±2.74
10 (Ac71-Ac80)	2.11±0.07	107.72±0.34	10.05±0.21	148.27±1.37
Average of 80 samples	1.82±0.02	95.30±1.60	12.00±0.28	141.07±2.02
Min. of 80 samples	0.54±0.04	29.46±0.26	3.39±0.09	39.95±0.40
Max. of 80 samples	2.81±0.38	141.36±0.49	30.13±0.93	312.37±0.73

Table 2

Pollen and physicochemical properties of *Robinia* honey samples

No. of Samples	Pollen (%) Mean	Pollen Conc. Mean	pH Mean±SD	Moisture content (%) Mean±SD
3 (Rb1-Rb7)	34.68	40041.60	3.84±0.02	17.63±0.19
3 (Rb8-Rb10)	32.69	24303.67	3.68±0.02	16.97±0.05
3 (Rb11-Rb13)	40.96	21457.82	3.71±0.01	17.33±0.05
3 (Rb14-Rb16)	52.36	29559.13	3.90±0.04	17.60±0.00
2 (Rb17-Rb18)	36.96	23887.25	3.90±0.02	17.60±0.00
Average of 14 samples	**39.7121**	**28132.9**	**3.80±0.02**	**17.41±0.06**
Min. of 14 samples	**20.41**	**4586.56**	**3.32±0.00**	**16.40±0.00**
Max. of 14 samples	**61.44**	**50214.5**	**4.05±0.07**	**18.25±0.21**

Continue of Table 2

No. of Samples	EC (mS/cm) Mean±SD	Free acidity (meq/kg) Mean±SD	Diastase activity Mean±SD	Invertase activity (U/kg) Mean±SD
3 (Rb1-Rb7)	0.34±0.01	5.91±0.17	8±0.09	23.05±0.67
3 (Rb8-Rb10)	0.29±0.00	7.94±0.17	8±0.08	28.43±0.45
3 (Rb11-Rb13)	0.29±0.00	8.15±0.02	8±0.12	10.73±0.34
3 (Rb14-Rb16)	0.35±0.01	8.09±0.12	10±0.16	13.54±0.87
2 (Rb17-Rb18)	0.40±0.04	11.05±0.16	6±0.12	9.06±0.56
Average of 14 samples	**0.33±0.01**	**8.03±0.12**	**8±0.11**	**17.53±0.58**
Min. of 14 samples	**0.11±0.00**	**4.75±0.21**	**5±0.13**	**3.26±0.24**
Max. of 14 samples	**0.48±0.09**	**15.20±0.31**	**12±0.17**	**55.26±0.40**

3.1.1. Qualitative pollen analysis. Pollen concentration values in 80 *Acacia* honey samples ranged from 2690.06 in sample Ac5 to 499640.00 in sample Ac26 (Table 1). Fourteen of them (17.50%) classified in group I (< 20 000 grains) (Figure 3). These samples may have been pressure-filtered, derived from floral sources that produced little pollen or partly produced by sugar-feeding of bees following the method of Maurizio (1975). Fifty one honey samples (63.75%) were categorized in group II (20,000-100,000 grains). In this respect these samples were regarded as "normal" because they were produced from normal floral sources (Crane, 1975). Fifteen samples (18.75%) were classified in group III (100,000-500,000 grains), indicating that floral sources are high pollen producers, or indicating that combs containing pure pollen were included in the extraction process. Honeys of group IV and V were not present in the samples. These are the ones with high pollen concentrations between 500,000 and 1,000,000 grains/10g, or higher respectively. The absence of such groups in the current study may be due to the authenticated pure honey samples, which were obtained directly from honey cells to ensure that the sample was not mixed with pollen stores in the comb (Maurizio, 1975).

Pollen concentration values in 14 *Robinia* honey samples ranged from 4586.56 in sample Rb8 to 50214.54 in sample Rb3 (Table 2). Three samples (21.43%) classified in group I (<20,000 grains). Most *Robinia* honey samples (11 samples, 78.57%) fall within the "normal" category (20,000 to 100,000 pollen grains in a standard 10 g sample) (Figure 3). No samples were categorized in group III, V and VI. Pollen concentration values were significantly ($p > 0.05$) greater in *Acacia* honey than in *Robinia*. In nature *R. pseudoacacia* produces low number of pollen, therefore the frequency of 20% - 30% of its pollen in honey sample are adequate to classify it as unifloral *Robinia* honey (Louveaux et al., 1978; Von der Ohe, et al., 2004).

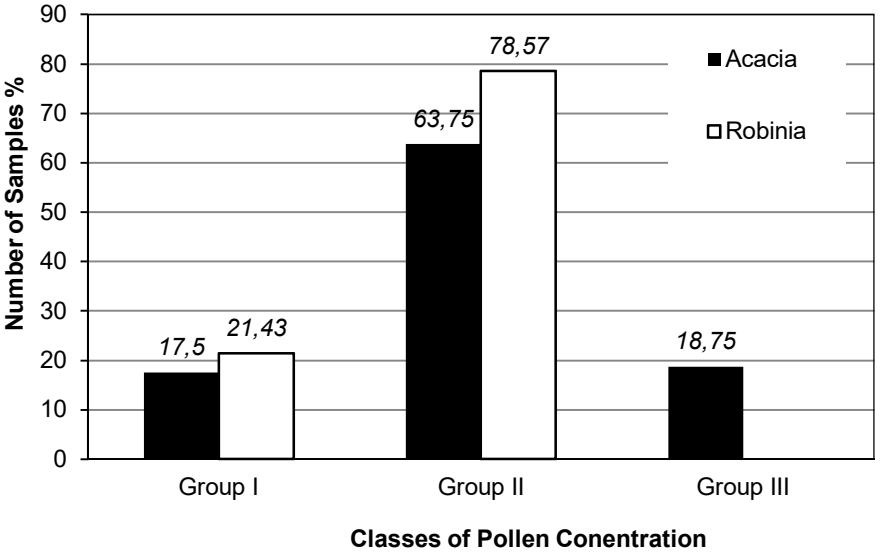

Figure 3. Distribution of samples (%) for pollen concentration in honey according to Maurizio's classes: Group I (<20,000 pollen grains); Group II (20,000-100,000 grains); Group III (100,000-500,000 grains per 10 g honey)

3.2. Physicochemical properties

One of the main objectives of this study was to differentiate between Omani *Acacia* honey (n= 80) and *Robinia* (n= 14) honey according to their physicochemical characteristics which are the major honey quality indicator parameters that include pH, moisture content, EC, free acidity, diastase activity and invertase activity.

3.2.1. pH. All *Acacia* and *Robinia* honeys analyzed were found to be acidic irrespective of their diverse geographical origin. The mean pH of *Acacia* honeys was 4.83 and its range was from 4.11 in sample Ac49 to 5.34 in sample Ac74 (Table 1). The mean pH of *Robinia* honeys was 3.80 and its range was from 3.32 in sample Rb8 to 4.05 in sample Rb14 (Table 2). The pH value range was larger in *Acacia* samples than in *Robinia* samples (Table 1 and Table 2). The range of both honey types complied with requirements (3.0–5.6) of GSO that were followed by the Directorate General for Specifications and Measurements, Ministry of

Commerce and Industry, Sultanate of Oman (GSO, 2008). They were also found to be within the general typical range of (3.42–6.10) as stated by (White, 1978). The current pH range of *Acacia* honeys were in agreement with the Saudi honey pH range (3.51–5.27) reported by Al-Doghairi, et al. (2007) and Alqarni, et al. (2012). It was also closer to the pH values of the Spanish honeys (3.63–5.01) (Cui, et.al., 2008). Fairly high pH values of *Acacia* honey might be due to the nature of the nectar, which is produced in hot and humid summer conditions in Oman (Sajwani et al., 2007). The acidic pH prevents the growth of many bacteria in honey (Gomes, et al., 2010). In this study, the pH of *Robinia* honeys ranged from 3.32 to 4.05. It was more or less similar to the pH values of European *Robinia* (3.7–4.2) reported by Persano Oddo and Piro (2004) and Serbian *Robinia* (3.89–5.05) honey (Lazarević et al., 2012).

The pH and acidity of honey may be due to the presence of some weak organic acids, such as gluconic acid, ascorbic acid, pyruvic acid, malic acid, citric acid and even acetic acid in equilibrium with their corresponding lactones or internal esters, and also to the inorganic ions, such as phosphate, sulphate and chloride (Echigo and Takenaka, 1974; Nigussie et.al., 2012). These aliphatic acids, particularly gluconic acid, contribute greatly to the flavor of honey by interacting with the flavors of other ingredients. In Omani honey, the most important organic acids found were gluconic acid, formic acid and acetic acid (Al Baz and Sabagh, 2000). Honey pH is of great importance during extraction and storage as it influences texture, stability and shelf-life (Baroni et al., 2009).

3.2.2. Moisture content. The moisture content of honey is another important factor for the shelf-life of honey contributing to its stability against fermentation and granulation during storage (Cereser Camara and Laux, 2010). It is well known that this parameter is related to the maturity and freshness of samples, regardless of their botanic origin or type of honey (Bentabol Manzanares et.al., 2011). This factor is affected by climate, harvest season, degree of maturity/ripeness reached in the hive, processing techniques, storage conditions, botanical origin of the sample and moisture content of original plant nectar (Özcan, Arslan et. al., 2006). Honey moisture content varies from year to year. High moisture content could accelerate crystallization in certain types of honey and increase its water activity to values where certain yeasts could grow. The undesirable honey fermentation during storage is caused by the action of osmotolerant yeasts resulting in the formation of ethanol and carbon dioxide. The alcohol can be further oxidized to acetic acid resulting in a sour taste and a runny texture with small bubbles, surface heaving or foaming (Sanford, 2009; Saxena et al., 2010). Moisture was not taken into account, as it is only related to the quality of honey and not to the botanical origin and therefore not useful for the differentiation among honeys.

Acacia honey samples showed the average moisture content of 16.75% and the range from 14.70 to 19.20% (Table 1). Robinia honey showed an average moisture content of 17.41% and ranged from 16.40 to 18.25%. In comparison, moisture content range of Acacia honey was wider then Robinia honeys nevertheless, both honey types meet the specification of CAC (2001) and GSO (2008) (Table 2). Acceptable levels moisture content of Acacia and Robinia honey samples were found in this study that reflect optimum harvesting and proper degree of maturity similar findings were reported for Saudi Acacia honeys (Alqarni et al., 2012). Relatively low moisture level of the current Acacia honey samples is at comparable levels of Egyptian honeys (20.12%) (Alqarni et al., 2012). This may be attributed to the hot and dry weather during April and May in the region of honey production. These results are in agreement with Alqarni et al., (2012) and Al-Doghairi et al. (2007). Viuda-Martos et al. (2010) reported high moisture content (≥23%) in some Mexican honeys and Terrab, et al. (2002) found similar trend in Moroccan honeys which is higher than the prescribed limit for the moisture content standards of CAC (2001). The high moisture values obtained were

probably because of the high rainfall recorded in these regions. In the present study, the water content range of Robinia honey (16.40 - 18.25%) was narrower than Acacia and was within the European Robinia range (14.7 - 19.6%) (Persano Oddo and Piro, 2004). Whereas Lazarević et al. (2012) recorded a wider range (13.90 - 20.57%) for Serbian Robinia honeys and Alqarni et al. (2012) reported moisture content of 21.68% for German commercial Robinia honey.

3.2.3. Electrical conductivity. The average EC values of Acacia honey was 1.82 mS/cm and the range was from 0.54 mS/cm in sample Ac49 to 2.81 mS/cm in sample Ac75. Only the EC values of samples Ac47 and Ac 49 were within the standard (not > 1.2 mS/cm) of GSO (2008) and CAC (2001). In the rest of the 97.5% samples these values were recorded out of the limits (Table 1). This could be due to two reasons: The first being the richness of Acacia honey in the pollen content as 63.75% of these samples belong to Group-II with 20,000-100,000 pollen grains per 10 g sample and these samples were regarded as "normal" following the terminology of Crane, (1975). The second reason might be due to the high content of minerals and organic acids in summer Omani honeys as found by Al Baz and Sabagh, (2000). Higher EC has been reported by El Sohaimy et al. (2015) in Yemen and Egyptian honeys (4.18±0.05, 1.98±0.03, respectively) which were also out of the GSO limits. They attributed this to the rich pollen and ash contents of these honey samples.

In *Robinia* honeys the average EC value was 0.33 mS/cm and it ranged from 0.11 mS/cm in sample Rb7 to 0.48 mS/cm in sample Rb13 (Table 2). All *Robinia* samples were within the limits of the CAC standards. *Acacia* honeys had a higher mean value than the *Robinia* honeys (Table 1 and Table 2). Saudi *Acacia* honey was similar to Omani's in the mineral contents as well as the range of EC, which was also higher (2.1–3.1 mS/cm) than the standard value (Alqarni et. al., 2012). They also noted that dark honeys (e.g., *Acacia* and linden) contain higher levels of microelements than light honeys (e.g., rape and *Robinia*) indicating *Robinia* honey is less ionic than *Acacia* honey. This explains its low EC value, in comparison to *Acacia*, as set in the limits of the CAC legislation. This range is similar to EC data recorded by Persano Oddo and Piro, (2004) and Lazarević et al. (2012) (0.09–0.230 mS/cm) and (0.10–0.690 mS/cm), respectively.

The EC of *Acacia* honey samples correlated positively and significantly ($P < 0.05$) with all other parameters studied (Table 3). Relatively weak correlations ($r = 0.240$ and 0.153) respectively were noticed for the moisture content and diastase activity, while moderate correlations ($r = 0.339$ and $r = 0.350$) respectively were obtained for the pH and invertase activity. EC showed a strong correlation ($r = 0.615$) with free acidity (Table 3) but there was a weak correlation between EC of *Robinia* honey samples and diastase activity ($r = 0.151$) and moderate correlation with pH ($r = 0.573$, $P < 0.05$) (Figure 4). No correlations were found between the EC of *Robinia* samples for the moisture content and invertase activity (Table 4).

The EC of honey is closely related to the concentration of mineral salts, organic acids, proteins, complex sugars and polyols content, the higher their content the higher the resulting conductivity (Bogdanov and Gallman, 2008). Since minerals are introduced into honey primarily with pollen, their content depends on the predominant pollen present in honey. Therefore, electric conductivity is a parameter which is very often used in routine honey quality control instead of the ash or mineral content. It can be considered a valid criterion for determining the botanical origin of a honey sample and differentiating honeys of different floral origins (Bogdanov et al., 2004; Ruoff et. al., 2006). EC value decreases with a decrease in the amount of pollen (Kaškoniene and Venskutonis, 2010). It is also a stable value for the same variety of honey, within a range of variability that remains practically invariable with treatments or storage (Krauze and Krauze, 1991).

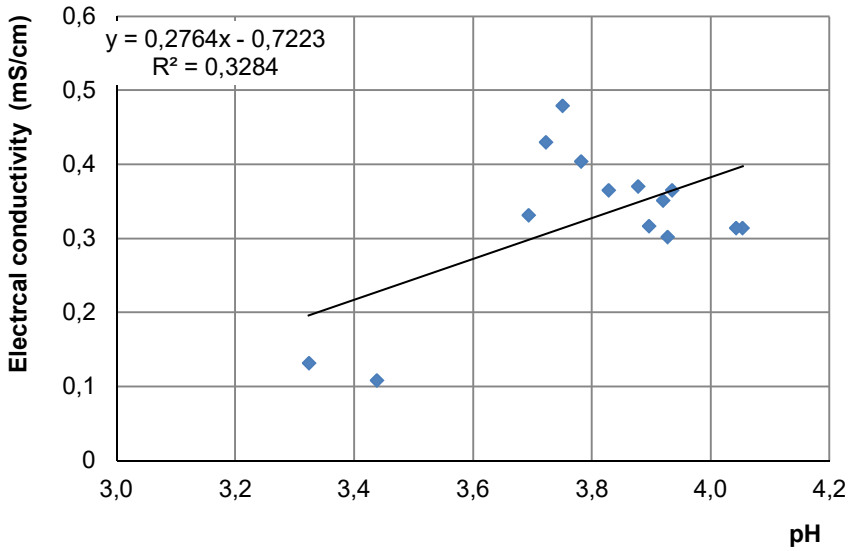

Figure 4. Correlation between pH and the electrical conductivity of 14 *Robinia* honey samples

3.2.4. Free acidity. All tested honeys were acidic; the range of free acidity for Acacia was from 29.46 meq/kg in Ac49 to 141.36 meq/kg in Ac4 with the average of 95.30 meq/kg (Table 1). Excluding Acacia honey samples Ac47 and Ac49, all the other 97.5% samples' free acidity values were > 50 meq/kg. These values were beyond the limits of GSO (2008). In Robinia honey samples, the free acidity ranged from 4.75 meq/kg in Rb3 and 15.20 meq/kg in Rb13. The mean was 8.03 meq/kg. The wide range may be due to variable flora in different production regions (Table 2). All the samples were within the limits of GSO, (2008) (Table 2) and within the range of the CAC criterion of European Robinia (4.5–17.9 meq/kg) (Persano Oddo and Piro, 2004). Table 1 and Table 2 showed wider free acidity range for Acacia honey than Robinia. Significant correlations were found between the Acacia honey free acidity and both the moisture content and EC ($r = 0.558$ and $r = 0.615$, $P < 0.05$), respectively (Figure 5, Figure 6 and Table 3).

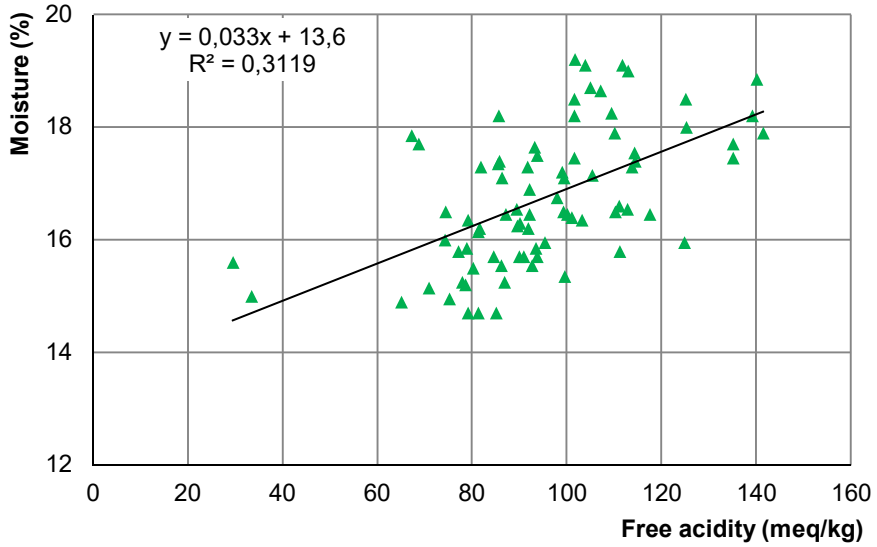

Figure 5. Correlation between free acidity and the moisture content of 80 *Acacia* honey samples

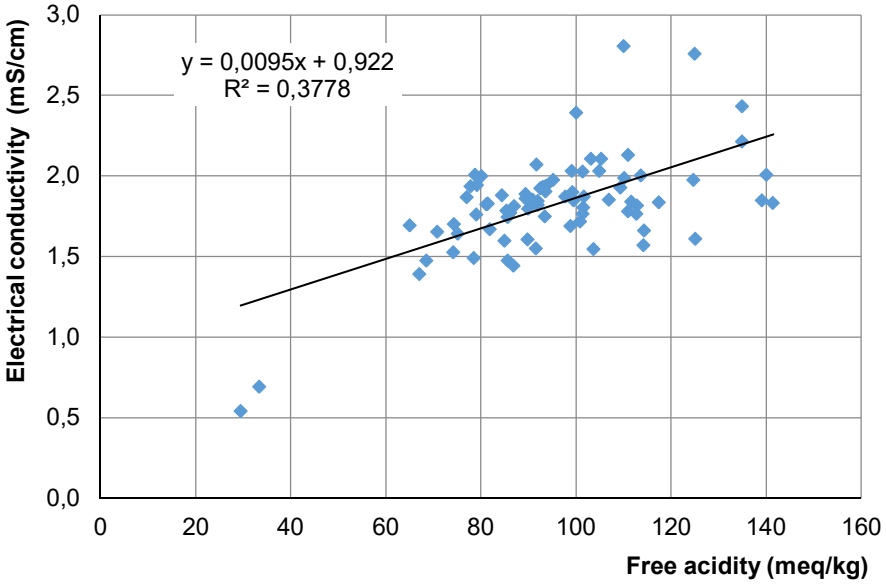

Figure 6. Correlation between free acidity and the electrical conductivity of 80 *Acacia* honey samples

Table 3

Correlation matrix showing the interrelation among physicochemical properties of 80 Omani *Acacia* honey samples

Parameters **	pH	Moisture content (%)	Electrical conductivity (mS/cm)	Free acidity (meq/kg)	Diastase activity (DN)	Invertase activity (U/kg)
pH	1.00	–	–	–	–	–
Moisture content (%)	NC	1.00	––	–	–	–
Electrical conductivity (mS/cm)	0.339	0.240	1.00	–	–	–
Free acidity (meq/kg)	NC	0.558	0.615	1.00	–	–
Diastase activity (DN)	NC	NC	0.153	0.160	1.00	––
Invertase activity (U/kg)	**0.213**	**NC**	**0.350**	**0.270**	**0.688**	**1.00**

** All the correlations were significant at 0.05 level (2-tailed). (NC) no correlation.

In *Robinia* honey samples, free acidity correlated significantly with EC ($r = 0.576$, $P < 0.05$) (Figure 7 and Table 4). All honeys are acidic with a pH value generally between 3.5 and 5.5, due to the presence of organic acids that contribute to honey flavor and stability against microbial spoilage. In honey the main acid is gluconic acid, which is found together with the respective glucono-lactone in a variable equilibrium (Bogdanov et al., 2004).

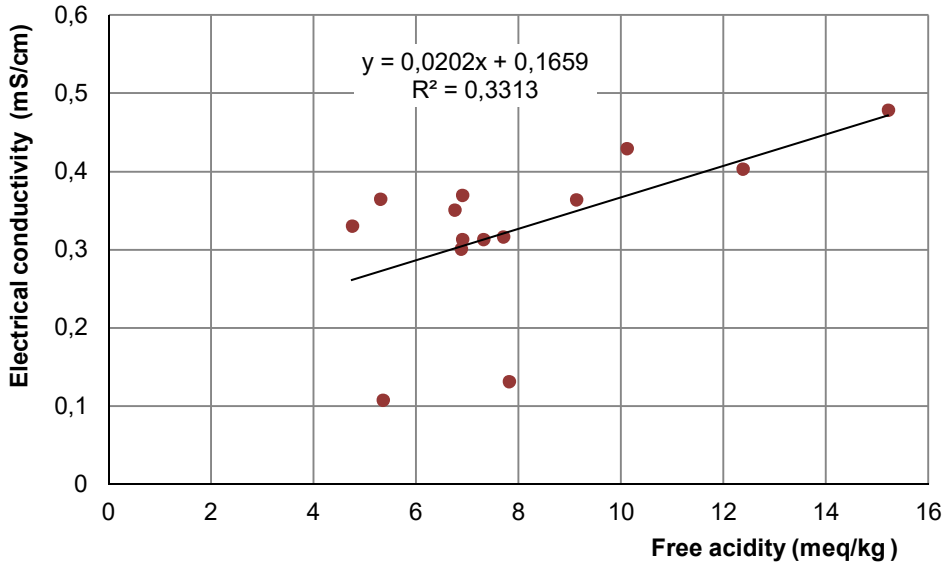

Figure 7. The correlation between free acidity and the electrical conductivity of 14 *Robinia* honey samples

Table 4

Correlation matrix showing the interrelation among physicochemical properties of 14 *Robinia* honey samples analysed

Parameters **	pH	Moisture content (%)	Electrical conductivity (mS/cm)	Free acidity (meq/kg)	Diastase activity (DN)	Invertase activity (U/kg)
pH	1.00					
Moisture content (%)	NC	1.00				
Electrical conductivity (mS/cm)	0.573	NC	1.00			
Free acidity (meq/kg)	NC	0.136	0.576	1.00		
Diastase activity (DN)	0.275	0.331	0.151	NC	1.00	
Invertase activity (U/kg)	NC	0.343	NC	NC	0.231	1.00

** All the correlations were significant at 0.05 level (2-tailed). (NC) no correlation.

The pH of a honey is not directly related to the free acidity because of the buffering action of the various acids and minerals present (Abu-Tarboush et al., 1993). Other factors can affect honey acidity, e.g. harvest seasons, floral types, content of enzymes and storage conditions (Perez-Arqillue, Conchello, A. Arino, and Herrera, 1994). Humidity and free acidity were found to be the most important parameters for classification of honey (Anklam, 1998). The free acidity of only samples Ac47 and Ac49 were within the limits of both CAC and GSO (not more than 50 meq/kg). Rest of the 97.5% *Acacia* samples were in the range of (65 - 141 meq/kg) (Table 1), although these samples were fresh and lacking undesirable fermentations.

Food control laboratories in Oman also recorded a wide range and high values of free acidity of *Acacia* honey which may reach to 100 meq/kg. Studies from Yemen and Saudi Arabia documented high free acidity of this type of honey, which are outside of the range of the current standards (AL-Zoreky et al., 2001; Alqarni et al., 2012). Al-Doghairi et al. (2007) found a wide range of total acidity between 9.12 - 93.02 meq/kg for Saudi honeys. The values for the free acidity ranged from 10.31 to 102 meq/kg as reported by (Terrab et al., 2002) in Moroccan honeys. Berg et al. (2008) found that the relatively low pH and high free acid content for New York buckwheat honey that may contribute to its ability to heal chronic wounds.

The high acidity in *Acacia* honey may be the result of the type of nectar produced in summer in plants growing in high salinity soils. It was observed that the honey obtained during the spring flowering season (February to June), is often more acidic than in the autumn season (personal observations; unpublished data). Al Baz and Sabagh, (2000) attributed the high acidity in *Acacia* honey to high humidity during the production season and the nature of the nectar produced by the *Acacia tortilis* plant. On the other hand, Tilbury (1980) and Costa et al. (1999) believe the high acidity in Brazilian honey is due to the hot climatic conditions, which favor the rapid growth of xerotolerant yeasts (e.g. *Saccharomyces rouxii*) that produce organic acids in honey as secondary metabolites, thereby raising the acidity.

Missio et al. (2016) and Alvarez-Suarez et al. (2017) reported that the high acidity can be an indicator of fermentation of sugars into organic acids which can affect the organoleptic characteristics of honey and its quality. While Vranić et al. (2017) reported that the variation in free acidity among different honeys can be explained by blossom origin, the presence of different organic acids or some inorganic ions, geographical origin or harvest season.

3.2.5. Diastase activity. The diastase activity of *Acacia* honeys was found to be in the range of 3 DN in sample Ac57 to 30 DN in Ac80 with an average of 12 DN on Gothe's scale. Out of 80 *Acacia* honeys 15 of them showed diastase activity > 8. Three of them (Ac12, Ac89 and Ac50) were from comb extracted honeys. The range of diastase activity in *Robinia* honeys was between 5 DN in Rb7 and 12 DN in Rb10. The average was 8 DN. Because *Robinia* honey has a low natural enzyme content (White, 1992), values of less than 8 DN are accepted in CAC standards. The diastase activity in ten samples had > 8 DN and four samples viz, Rb6, Rb7, Rb13 and Rb14 showed < 8. The range of diastase activity was wider in *Acacia* samples compared to *Robinia* (Table 1 and Table 2). Diastase (α-amylase) is one of the most important enzymes in honey added by the bees during the conversion of nectar into honey. It converts starch to short-chain sugars. Therefore no starch is found in honey. The diastase content varies according to the floral source, long storage periods and exposure to high temperatures (White and Bryant, 1996).

Heating honey denatures the enzyme, therefore the legislation has set a minimum level (< 8 DN) for diastase activity (Codex Alimentarius Commission, 2001). It is undesirable to have either very low or very high diastase activity in honey (Tolon, 1999). The latter may occur due to the formation of acid and may result in fermentation (Yardibi and Gumus, 2010). The current study showed a wide range of diastase activity in *Acacia* honey samples from 3.32 to 30.13 DN. This observation is common in the fresh, unheated honeys as reported by White (1994) and indicates their variable geographical and biological origins (White and Bryant, 1996).

Our results illustrated that the diastase activity in 81% *Acacia* honeys was > 8 DN, whereas only 19% of the samples shown < 8 DN. This was not caused by the aging, adulteration or heating of these samples since they were collected fresh from the beekeepers in the season and stored in glass bottles with tight caps in a freezer. Besides, heating honey is not usually practiced by the Omani beekeepers. Out of these 15 samples, 3 of them (Ac12, Ac30 and Ac50) were from comb honeys, which show natural low diastase activity (White, 1994). The low diastase activity might be due to the high temperature environment within the bee colonies. This explanation also gathers support from German and American investigators who observed that honeys from warmer regions and comb honeys could have low diastase activity (White, 1994).

Studies from Saudi Arabia, Algeria and Yemen also documented similar low diastase activity (< 8) in honey samples (Al-Khalifa and Al-Arify, 1999; Al-Zoreky et al., 2001; Chefrour et al., 2009) respectively. White (1992) explained the reason of low diastase which occurs naturally in some honeys. Since it is agreed that the enzymes are added by the honey bee during the collection and the ripening of the nectar to make it a thick consistency, also it is known that some nectars are naturally much thicker to start with than others, therefore some nectar types require less manipulation by the bees in the hive to attain that thick consistency. This results in the addition of lower levels of diastase and invertase and other materials by the bee. In the United States diastase activity is mainly controlled to ensure low diastase values because much of the honey supply is used in bakeries for mixing with starch-containing food ingredients and a high diastase number could cause poor bread texture (White, 1992). A low diastase activity range (5–12 DN) was found in *Robinia* honey samples,

compared with the *Acacia* honey samples. This was within the range (3.1 - 20.4 DN) of European *Robinia* honeys found in the database of the IHC (Persano Oddo and Piro, 2004). The low diastase activity (< 8) is accepted by EUC and CAS because *Robinia* honey is classified as a low diastase containing honey (Persano Oddo and Piro, 2004). White (1992) advised against using diastase activity as a basis for measuring honey quality because of its uncertainty due to its extreme variation in the level of its starting point. The diastase activities in honey vary in wide limits depending on botanical origin of honey. The enzyme has no nutritional basis as a dietary requirement; therefore, diastase measurement should not be used as a regulatory standard for honey quality. This recommendation is respectfully made to Saudi Arabian and other Gulf authorities dealing with honey imports.

3.2.6. Invertase activity. *Acacia* honeys were in the range of 39.95 U/kg in sample Ac49 to 312.37 U/kg in sample Ac24 with an average of 141.07 U/kg (Table 1). The range of invertase activity in *Robinia* honey was between 3.26 U/kg in sample Rb7 to 55.26 U/kg in sample Rb4 with an average of 17.53 (Table 2). Significant correlation was found ($r = 0.688$, $P < 0.05$) between diastase and invertase activities in *Acacia* honey samples (Figure 8 and Table 3).

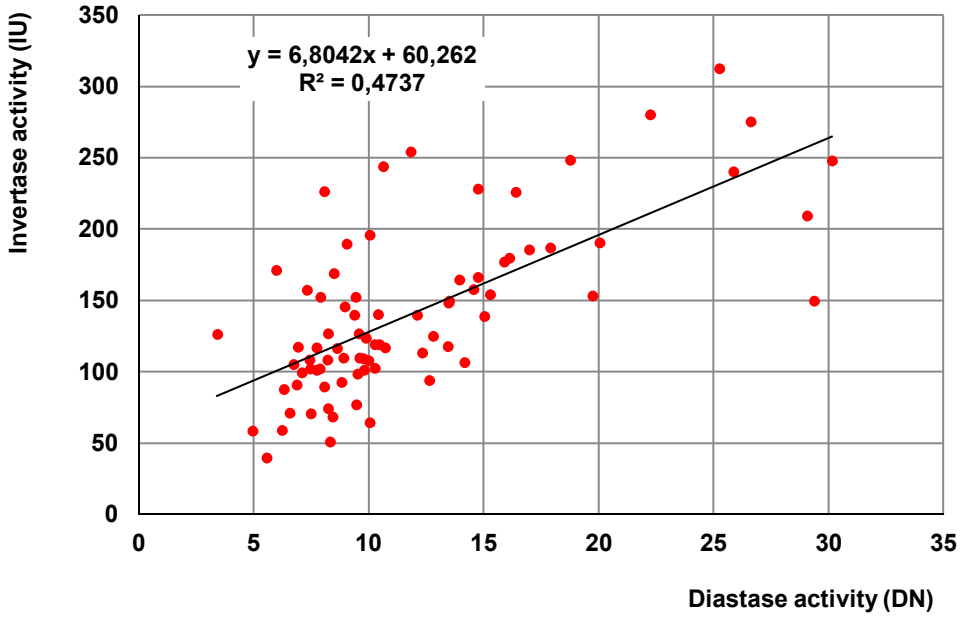

Figure 8. The correlation between diastase and the invertase activities of 80 *Acacia* honey samples

However, there was weak correlation ($r = 0.229$, $P < 0.05$) (Table 4) for these parameters in *Robinia* honey samples. Invertase (α-glucosidase) is the enzyme added to the nectar by the bee that converts the sucrose of the nectar to glucose and fructose, a vital step in the ripening of nectar to honey. Invertase is more susceptible to temperature than diastase. The activity of this enzyme decreases depending on the temperature and time of honey processing (White,

1992). Similar to diastase, it is hard to interpret the results of invertase activity in terms of freshness, since the initial value is unknown (Dinkov and Vashin, 2001). There were significantly ($P < 0.005$) variable activities of this enzyme in the studied *Acacia* honey samples (40–312 U/kg). Al-Khalifa and Al-Arify (1999) recorded the range of invertase activity 26.7 to 76.7 U/kg for three *Acacia* honey samples from Saudi Arabia.

Invertase activity ranged (3.26–55.26 U/kg) in *Robinia* samples which is within the permitted range (3.4 – 107.5 U/kg) of European *Robinia* honeys found in the database of IHC (Persano Oddo and Piro, 2004). It was observed that the range of invertase activity of *Acacia* samples was larger than the *Robinia* samples. In addition, both ranges of *Acacia* and *Robinia* were wide. This variation among honey samples is due to a number of factors such as enzymatic activities, concentration and composition of the nectar, amount of sucrose in honey, and even the age of honeybees. Therefore, honeys from rich nectar sources such as *Robinia* often contain low natural enzyme activities (White, 1994). All honeys with high enzyme content are produced in summer when brood rearing is less intensive and foragers are predominant. Therefore the nectar collection time (the physiological state of the colony) and consumption of pollen by bees also have influence on the enzyme activities (Huang and Otis, 1989).

3.2.7. Correlations amongst the quality control criteria. The correlation matrix (Table 3 and Table 4) showed a significant correlation between the quality control criteria. This study verified uniform pattern of the results for all the parameters studied. For example, *Acacia* honey sample Ac49 was collected from a commercial apiary that fed sugar to the bees for a long time that was reflected in its quality. The results of this sample showed the lowest values of pH, EC, free acidity and invertase activity (4.11, 0.54 mS/cm, 29.46 meq/kg and 39.95 U/kg, respectively) in comparison to the rest of the samples. The EC of *Acacia* honey samples was the only criterion found to correlate significantly and positively with pH, moisture content, free acidity, diastase and invertase activities. This may indicate the influence of these parameters in raising the EC of this honey. The significant and positive correlation between free acidity and EC of *Acacia* honey may indicate the richness of this type of honey in minerals and organic acids. All of these point to its rich nutritional and medicinal value.

Many investigators such as Persano Oddo et al. (1999) and Serrano et al. (2007) have reported a highly significant and positive correlation between diastase and invertase activities; at the same time demonstrating the correlation between the two enzymes, showing that honeys with a low content of invertase also have a low content in diastase, and vice versa. This correlation maybe useful in excluding honeys in evaluation of adulteration. In the current study, the correlation between diastase and invertase in *Acacia* honey was found to be significant ($P < 0.05$) with the coefficient of correlation ($r = 0.688$), which was similar to that reported by Horn and Boehm (2004) ($r = 0.700$) but lower than those obtained by Persano Oddo et al. (1999) ($r = 0.835$). The low correlation coefficient between both enzymes found in tested *Robinia* honeys ($r = 0.2$) was similar to the reports of Vit and Pulcini (1996) and Bentabol Manzanares et al. (2017). The low correlation may be because of the low content of diastase in these types of honeys probably due to the high nectar flow that does not allow bees to adequately process it (White, 1994). Data in this study are in agreement with the reports of (Persano Oddo et al., 1999) that these enzymes may not provide useful information about the freshness of honey because they are variable from one type of honey to another.

4. Conclusion

This study was undertaken to elucidate the true *Acacia* honey from white *Acacia* (*Robinia*) honey. It is highly recommended to label them with specific names, which can be used by both scientific and public communications. We suggest the name "*Acacia"* for *Acacia* spp. honeys and "*Robinia"* for *Robinia pseudacacia* honey. This suggestion is put forward to honey regulators such as the CAC, IHC, and EUC directive relating to honey.

The quality control criteria showed that Omani *Acacia* honey possesses relatively higher values of physicochemical parameters, which mostly meet the major permitted specifications. The EC of this honey was found to correlate significantly with pH, moisture content, free acidity, diastase and invertase activities. This may point out the influence of these parameters in raising the EC value indicating the richness of *Acacia* honey with mineral and organic acid contents, which may increase its nutritional and medicinal value. It was found that most of the *Robinia* honey samples purchased from the local markets in Oman met the national and international standards. This may satisfy the consumer when going for this product safety although its quality is lower than that of Omani *Acacia* honey.

Some criteria of *Acacia* honey such as EC and free acidity were not within the range of the currently available standards. This shows that Oman needs to build its own honey database and standards for the regional honeys. The values in the current standards are not in accordance with those obtained from honey from the Arabian Peninsula, which, were formulated based on European and imported honeys. Originally, they were promulgated during the 1960s.

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Improving technology of producing non-alcoholic drinks using non-traditional raw materials

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Abstract

Introduction. The technology for the production of soft drinks using non-traditional raw materials with the aim of improving and expanding the range of products was investigated.

Materials and methods. Non-traditional raw materials were used to create the basis of a soft drink, in particular, strawberry and raspberry extract. The number of polyphenols in the objects of study were determined by spectrophotometric method. The optical density was measured in a cuvette with a layer thickness of 10 mm on a SF-46 spectrophotometer.

Results and discussion. The content of phenolic compounds is crucial for the stability of beverages. The using of morphological particles of raw materials makes it possible not only to improve the sensory properties of beverages, but also to extend their stability. Raspberry powder extract (2.30 and 1.02) had better phenolic compounds and rutin content than strawberry powder extract (1.50 and 0.30).

Available data indicate that the vegetative parts of plants contain no less biologically active substances, and sometimes even more than fruits, berries and vegetables, and their using allows to get concentrates and drinks from them with soft, piquant, harmoniously individual flavor and aroma.

Focusing on the rich content of valuable components, the leaves and stems of raspberries and strawberries were investigated for the using of additives to the concentrate of soft drinks.

Extract, which is prepared by boiling the chopped leaves and twigs in water for 3 minutes, has better sensory properties compared to other samples, so this method of preparing raspberry extract is optimal. Strawberries were excluded from the experiment due to the rich grassy tones in the taste and the corresponding aroma.

0.75 g and 1.0 g in 100 cm3 of raspberry extract are best suited for use in order to create the basis for a soft drink.

Conclusions. Using of extracts of non-traditional plant materials will help to improve the sensory properties of the soft drink and expand the range.

Introduction

The production of soft drinks is characterized by an extremely wide variety of raw materials [1] The use of juices, concentrates, infusions and extracts of vegetable raw materials, materials, flavors, emulsions, aromatic bases of other raw materials [3] The consumption of soft drinks not only compensates for the loss of moisture and salts by the body, but also enriches it with the vital biologically active substances [5]The growing consumer demand for quality beverages implies a constant search for technology improvements and the quality of finished products [6]

The purpose of research was to establish the perspective and feasibility of obtaining a drink enriched with biologically active substances of non-traditional raw materials.

Literature review

In the analysis of the development of the production of soft drinks in recent years, there is a clear tendency for their "naturalization" – from the use of the bases of artificial origin to identical natural and natural. Thus, the strategic direction of the industry development is the use of natural ingredients, which is in line with the improvement of existing technologies and the introduction of new ones [1].

One of the most important problems of the development of the beer and soft drinks industry is to improve the quality of products, marketing competitiveness, primarily cost reduction and improvement of the range [1] It can be achieved by developing and implementing production aimed at reducing the duration of the main production stages and improving the quality of beverages without significant costs of material and energy resources [1] One of the ways to solve this problem is to optimize the technology of soft drinks by using the so-called “basics” – basic intermediates, parts with the main set of prepared ingredients, improving the composition of the drink, providing it with preventive and health properties [2].

Basics for beverages are prepared mainly using concentrated citrus juices [2]. Usually used six times concentrated juice with a dry matter content of up to 65%, pulp not more than 5%. If necessary, add dyes, acid and preservatives [2].

Concentrates for soft drinks, as a rule, consist of 2 parts: aromatic and extractive [2]. The aromatic part A is prepared by dissolving the essential oils in alcohol. The strength of the aromatic part A is not less than 93% [2].

The extractive part B is prepared by mixing hydroalcoholic extracts of the herb St. John’s wort, licorice root, Eleutrococcus (or levzey), dye and citric acid. This technology is energy and material costly [3] In addition, it requires a long time and a large amount of staff [3].

Development of technologies using the basics is relevant, therefore, their use in the beverage industry is cost-effective, as the technology is simplified, the loss of raw materials is reduced.

Within the framework of the considered trends, special relevance is development of various concentrated bases for non-alcoholic drinks. The solution of these tasks can be carried out in two directions: [4]

– the creation of efficient technologies for the processing of vegetable raw materials, provide maximum enrichment of the resulting infusions and extracts natural extractives. Creature concentrates based on extracts should be provided by different forms: liquid, highly concentrated, pasty, powdered, in the form of granules, etc;

– enrichment of concentrated bases with essential nutrients and their premixes.

The latter direction has practical application in the development of soft drinks of various functional orientations [4].

The creation and improvement of technologies of concentrated bases on a natural basis is a prerequisite for the stable development of production of high-quality soft drinks.

Important is the integrated use of plant materials with the study of its active and minor components, ensuring the direction of the functional properties of concentrates and drinks based on them [4].

It was investigated the extraction of biologically active substances of lemon balm and calendula, hawthorn of red-blooded, black-fruited rowan, rose hips [5], medicinal sweetcorn, common yarrow, rose hips, hawthorn, roots of malt root [6], linden and elder flowers, raspberry, strawberry, currant, lemon balm and blueberry shoots [7] for the development of non-alcoholic drinks.

Publications on sweet potato studies show that the content of vitamins and minerals in it are comparable with various fruits [8] According to research sweet potatoes are rich in dietary fibre, minerals, vitamins, and antioxidants, such as phenolic acids, anthocyanins, tocopherol and β-carotene. They are an excellent source of vitamin A and a good source of potassium and vitamin C, B6, riboflavin, copper, pantothetic acid and folic acid. The total antioxidant capacity determined by Oxygen radical absorbance capacity values of purple-fleshed sweet potatoes were comparable with those of fruits (apples, apricot, avocado, cherries, grapefruit, orange, pears) and vegetables (broccoli, cabbages, eggplants, lettuces). Scientists reported that sweet potato cultivars whose roots are used for a beverage, paste, powder, an alcohol drink and a natural colorant have been developed. Consumption of non-carbonated drinks has become increasingly important. A number of fruit drinks manufactured from fruit juice and other natural ingredients are popular and are sold worldwide. Vegetable juices are also available. The demand for these drinks and beverages is largely based on their nutritive value, flavor, aroma and color. The quality of the sweet potato non-alcoholic beverage is within the acceptable quality range [8].

Berries and their products are very often recognized as “superfoods” [9] They possess high concentrations of phenolic compounds, which have been found in in vitro and in vivo studies to possess a range of biological activities, including anticancer and antiplatelet activities, as well as antioxidant properties [20]. However, these compounds may not influence the levels of oxidative stress biomarkers, and may even have prooxidative effects. In addition, the precise biological activities of berry phenolics are dependent on a range of factors including the class of phenolics, their concentration, the type of berry and even the form consumed, be it fresh berries, juice, wine, jam, oil or medicinal products. The addition of non-traditional vegetable raw materials not only expands the range, but also improves the performance of beverages, increases stability, gives the drink a feature that sets it apart from other beverages [9].

Available literature data [10] show that the vegetative parts of plants contain biologically active substances not less and sometimes more than fruits, berries and vegetables, and their use allows to get concentrates and drinks from them with soft, savory, harmoniously-individual flavor and aromatic.

Unfortunately, the problem of the integrated use of this raw materials is practically not solved.

Focusing on literary sources and the rich content of valuable components, the leaves and stalks of currant, raspberry and sea buckthorn were examined for the use of the additive as a concentrate soft drinks [10].

European raspberry, common raspberry or just raspberry (Rubus idaeus, local names: red raspberry, raspberry, bearberry) – bush family pink (Rosaceae) 1-2 m tall with annual vegetative shoots and lignified biennial stems that form flowering groves.

Raspberries contain pectins, which help remove various harmful substances from the body through the intestines, including cholesterol, and radioactive elements, so raspberries are recommended for people working in various heavy enterprises. Coumarins contained in raspberries improve blood clotting, and reduces the level of prothrombin [10].

Coumarins are concentrated in the leaves and in the branches. Anthocyanins strengthen capillaries, and reduce the tendency to sclerosis. Phytosterols reduce likelihood of atherosclerosis. Potassium contained in raspberry helps to improve the situation of people with a heart condition, as well as potassium [10].

There is iodine in raspberries, which has a beneficial effect on bronchitis, causing expectoration [10].

Strawberry is a very common berry. One of the organic acids found in strawberries neutralizes cancerous effects when smoking tobacco [12] .

Broth leaves (Folia) strawberries have long been used as a good remedy for insomnia. Strawberry is a good prophylactic against atherosclerosis and hypertension, it normalizes blood pressure and metabolism [12].

Tea with raspberries, strawberries or with their leaves, brewed together with tea leaves soothes pains in the stomach and in the intestines during gastritis. Raspberries contain a lot of copper, and copper is a part of many antidepressants, so raspberries should be eaten by those people who have a job associated with great nervous tension. Due to the fact that raspberry contains vitamin A, E, PP, C increases the tone and improves well-being [12].

The chemical composition of raspberry and strawberry leaves is rich: anthocyanidins and anthocyanins – water-soluble flavonoids (powerful antioxidants), phytosterols (kaempferol), tannins, essential oils, borneol, anthocyanins: callistephin, chrysanthemum, volatile compounds: verbenone, citronella, organic acids (citric, malic, cinnamic, hydroxybenzoic, gallic, chlorogenic, salicylic) and their esters, as well as ellagic acid, which is a natural phenolic antioxidant. Ascorbic acid, or vitamin C, is a strong antioxidant and chelating agent. As a result of the literature review and taking into account the importance of using plant extracts, we came to the conclusion that the use of raspberries and strawberries, namely extracts of leaves and twigs rich in phenolic components and coumarins and vitamins (Vit. C, Rutin) would be appropriate in the manufacture of soft drinks (Figure 1, 2) [13].

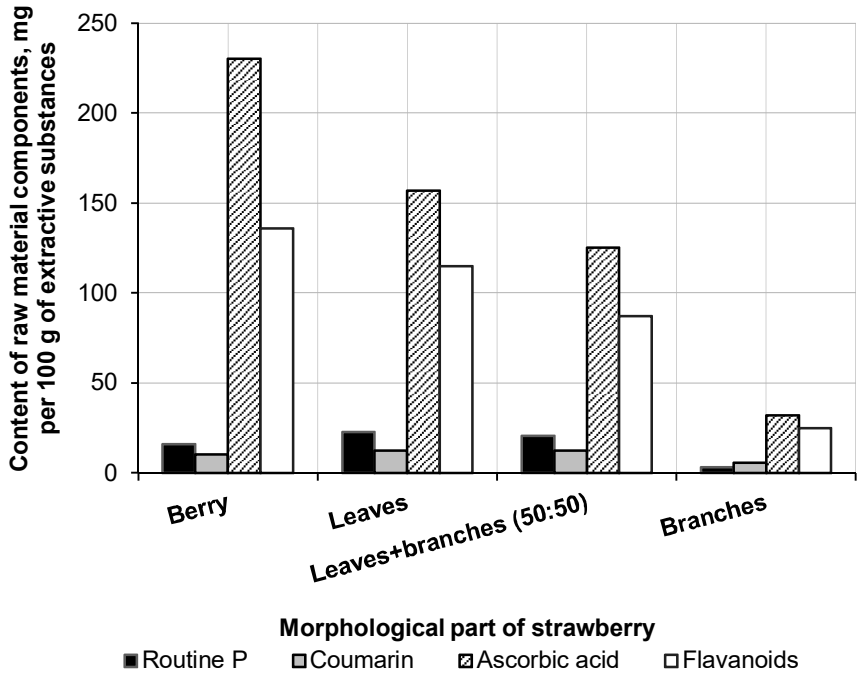

Figure 1. Content of strawberry components

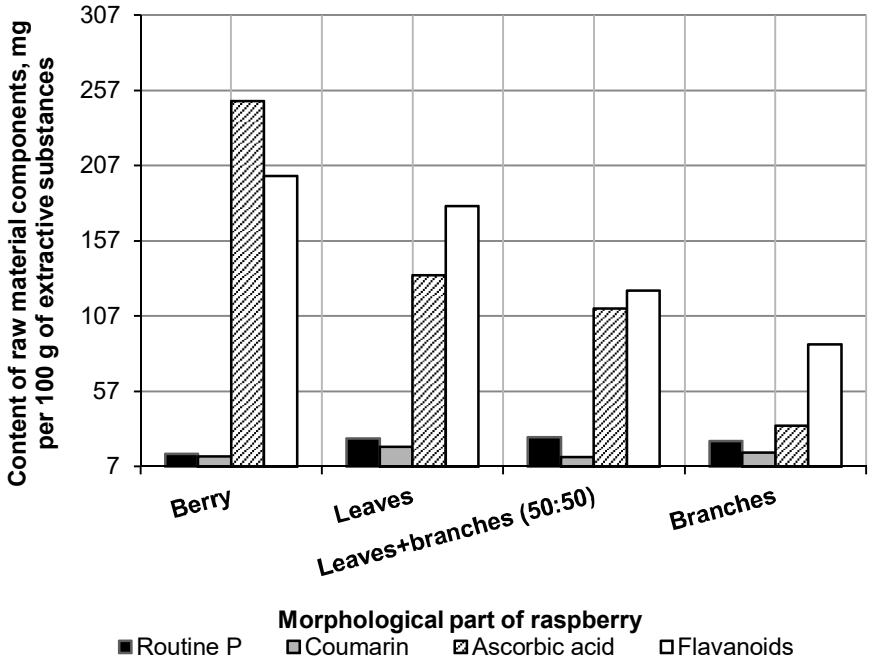

Figure 2. Content of the components of raspberry

Materials and methods

To prepare the sample for analysis, the samples were ground to a powder state, after which they took a sample of 1.0000 g, poured 50 ml distilled water heated to 100 °C. Maintained for 5 minutes, then filtered. Next, the aqueous extract was brought to a boil and boiled for 3 to 5 minutes. The next step was the exposure of the FDP in 55% water-alcohol mixture for 2 days and then the FDP in 70% water-alcohol mixture for 2 days [14].

Determination of the pH. 100 ml of sample is poured into a measuring glass, shaking for 10 min and immersing the pH electrode in the solution [15].

Titrated acidity. 100 cm^3 of distilled water and 10 cm^3 of sample are poured into a conical flask with a capacity of 250 cm^3. 4-5 drops of an alcoholic solution of phenolphthalein with a mass concentration of 10 g/dm^3 are added to the solution and titrated with a solution of sodium hydroxide at a concentration of 0.1 mol/dm^3 until a pink color appears, which does not disappear for 30 s [15].

Determination of the amount of polyphenols. For a preliminary assessment of the qualitative composition of water or alcohol extract of raspberry and strawberry (leaflets and shoots), generally accepted qualitative reactions were performed, followed by determination of the phenolic components by spectrophotometric method [14]. The determination of the amount of polyphenols was performed spectrophotometrically by measuring the absorption index of the test sample after adding Folino-Checalteu reagent and 20% sodium carbonate solution [16]. Optical density was measured in a cuvette with a layer thickness of 10 mm on a spectrophotometer SF-46 at the appropriate wavelength [16]. Recalculation of the percentage of the amount of polyphenols was carried out on chlorogenic acid.

The determination of the amount of soluble solids. The concentration of soluble solids in samples was measured using refractometer. On the lower prism of the refractometer, 2-3 drops of the test liquid are applied with a glass rod. The upper part of the prism is lowered, tightly applied to the lower stationary part of the prism and counted on a refractometer scale [15]

When calculating the readings, it is necessary to note the temperature at which the tests are carried out. If the temperature differs from 20 °C, make the appropriate amendment [15].

Results and discussion

The content of phenolic compounds, including rutin in powders obtained from raspberries and strawberries are presented in Table 1.

The results of total phenolic content proved that raspberry and strawberry powder, which were keeping the FDP in 55% water-alcohol mixture for 2 days contain a highest amount of these compounds. But alcoholic extracts are material-intensive.

The content of phenolic compounds is crucial for the stability of beverages. The use of morphological particles of raw materials makes it possible not only to improve the sensory properties of beverages, but also to extend their stability.

Sample No. 2, which belongs to the extract of water powder from morphological particles of raspberry and strawberry, brought to a boil and boiled for 3–5 minutes on the content of phenolic components and aroma was suitable for further research [16, 20].

Table 1

Content of phenolic compounds

Processing option	Raspberry powder		Strawberry powder	
	Amount of phenol	Rutin	Amount of phenol	Rutin
Water extract, heated to 100 ^{0}C, sustained 10 min	2,3	1,02	1,5	0,3
The water extract, brought to a boil and boiled for 3 to 5 minutes	2,38	1,1	1,67	0,36
Keeping the FDP in 55% water-alcohol mixture for 2 days	2,63	1,84	1,8	0,64
Keeping the FDP in 70% water-alcohol mixture for 2 days	2,4	1,8	1,67	0,58

Next, we conducted a study of the time of extraction by boiling, as evidenced by the data of Table 2.

Table 2

Sensory characteristics of raspberry extract in boiling extraction

Duration of boiling, min	Colour	Aroma	Taste
1	Light, straw yellow, poorly saturated, without extraneous opacities	Weak with hints of spice	Weak, unsaturated, grassy
3	Light, straw-yellow, medium intensity, without other opacities	Medium intensity, there are shades of spices and fresh hay	Pleasant, medium rich shades of meadow herbs
5	Saturated, straw-yellow with a greenish tinge, without extraneous opacities	Intense, pronounced shades of spices and fresh hay	Saturated, with a slight bitterness, with pronounced tartness
8	Saturated, straw yellow, with a greenish tint, without extraneous opacities	Intense, there are shades of burnt	Saturated, with unpleasant bitterness and tartness

According to the sensory evaluation of the investigated samples of raspberry powder extract, which are listed in Table 2, it was determined that the extract, which is prepared by boiling crushed leaves and twigs in water for 3 minutes, has better sensory properties compared to other samples, therefore this mode of preparation of raspberry extract is optimal. The strawberries from the experiment were excluded from the rich herbal tones in the flavor and the corresponding flavor.

Table 3

Physical and chemical indicators of raspberry extract when extracted by boiling for 3 minutes

Duration of boiling, min	pH	Content of dry substances, %
1	6,81	0,5
3	6,77	0,6
6	6,81	0,6
9	6,73	0,6
11	6,57	0,7

Samples were prepared according to the scheme below. Aqueous extract of aromatic raw materials were crushed, sieved to a homogeneous mass and took the sample in the amount of 0.25; 0.5; 0.75; 1.0; 1.25 g per 100 cm3 of water, boiled for 3 minutes. The data of sensory analysis entered in Table 4.

Table 4

Sensory characteristics of the extract of raspberry leaves and twigs

Amount of extract, g	Appearance	Transparence	Aroma	Taste
0,25	Color light straw transparent	Transparent, without sediment	Straw transparent, no sediment grassy aroma of forest herbs	Straw, grassy, weak taste of grass
0,5	Straw	Transparent, without sediment	Herbal	Forest scent
0,75	Amber	Transparent, without sediment	Herbal, more intense than the previous one	Harmonious herbal with a touch of meadow herbs
1,0	Amber	Transparent, without sediment	Herbal, intense	Intense herbal
1,25	Intensive honey	Transparent, without sediment	Intense, intensely herbal	Herbal, with bitterness

General characteristics of solutions: with increasing concentrations, the color becomes more intense, all solutions are transparent, without sediment, the aroma increases, the taste becomes more intense. According to the results of the experiments, it was established that 0.75 g and 1.0 g in 100 cm^3 of raspberry extract meets our goals best. For the convenience of preparing solutions, we select a sample of 1.0 g in 100 cm^3 (1% aqueous solution).

In order to improve and expose the sensory characteristics of soft drink, we have suggested adding a poly-malt extract to the recipe.

Available data indicate that the vegetative parts of plants contain no less biologically active substances, and sometimes even more than fruits, berries and vegetables [17], and their using allows to get concentrates and drinks from them with soft, piquant, harmoniously individual flavor and aroma.

Preparation of an aqueous solution of poly-malt extracts: in chemicals contained in substances quantitatively transferred into a volumetric flask per 100 cm^3 and brought up to the mark with distilled water. Sensory indicators were determined.

The sensory analysis data are entered in Table 5.

Table 5

Sensory characteristics with the introduction of poly-malt extract

Amount of extract, ml	Appearance	Transparence	Aroma	Taste
1,5	Light, transparent	Transparent, without sediment	Honey, with a touch of herbs	Honey, slightly sweet
2,0	Light, transparent	Transparent, without sediment	Honey, with a touch of herbs	Honey, slightly sweet
2,5	Light, transparent	Transparent, without sediment	Honey, with a touch of herbs	Honey, slightly sweet
3,0	Light, transparent	Transparent, without sediment	Honey, with a touch of herbs	Honey, slightly sweet, but more intense than the previous one
3,5	Light, transparent	Transparent, without sediment	Honey, with a touch of meadow grass	More opened bouquet
4,0	Light, transparent	Transparent, without sediment	Honey, with a touch of herbs	Opened bouquet, as in the previous sample

General characteristics of solutions: all solutions are transparent, without sediment, despite the amount of extract (from 0.25 to 8.0 g), the intensity increases with a large amount of extract. The aroma is enhanced with an increase in quality, but its shades change: up to 5 g per 100 cm^3 – the characteristic shades of herbal and honey, after 5 g – possible malt shades of taste. Taste of honey participation in all samples. At the same time in a large amount of extract, sweetness grows, however, in samples 9 and 10 are sensitive to cold sharp shades, both in taste and in flavor.

To determine the stability of the aqueous solution of the extract, the best samples (sample with an amount of extract of 3.0 g and a sample with an amount of extract of 4.0 g) are kept in a refrigerator at room temperature for 3 days.

In the refrigerator, the samples became less turbid. Not steady precipitate falls out. After filtration, the filtrate was stable, a precipitate was not formed during storage for 3 days in the refrigerator.

As a result, we obtained a base consisting of a polysod extract and a 1% raspberry solution, and a glucose-fructose syrup of a certain concentration was chosen for sweetening.

Creation and improvement of technologies of concentrated bases on a natural basis is a prerequisite for the production of high quality soft drinks. According to the results of research, the selected recipe of the drink "With the taste of honey".

Table 6

Formulation per 1000 l

Raw material	Unit of measurement	Solids content in raw materials,% of the mass.	Consumption rate	Content of dry substances according to the norms of consumption, % mass
Glucose fructose syrup	kg	65,0	38,00	24,70
Poly malt extract	kg	75,0	75,18	56,39
Citric acid	kg	90,97	1,08	0,98
Infusion of raspberries (branches, leaves)	kg		0,30	
Flavor "Isindi"	kg		0,20	
The amount of acid, made with the Poly malt extract	kg	0,05	75,18	0,04
Water	dm^3	up to 1000.00		
Carbon dioxide	kg		4,15	
Total solids in the drink	kg			82,07

General characteristics of the solutions: all the solutions are transparent, without sediment, despite the amount of extract (0.25 to 8.0 g), the intensity increases with a large amount of extract. The aroma increases with increasing quality, but its shades change: up to 5 g per 100 cm^3 - characteristic shades of herbal and honey, after 5 g – malty flavors of taste

are possible. Taste of honey involvement in all samples. At the same time sweetness increases in a large amount of the extract.

To determine the stability of the aqueous solution of the extract, the best samples (sample with extract amount of 3.0 g and sample with extract amount of 4.0 g) are stored in the refrigerator at room temperature for 3 days.

In the refrigerator, the specimens became less cloudy. Resistant sediment is not maintained. After filtration, the filtrate was stable, the precipitate was not formed during storage for 3 days in the refrigerator.

Conclusions

1. The use of unconventional raw materials, such as extracts of raspberry, strawberry, or sea buckthorn, will help to expand the range of soft drinks.
2. Raspberry and strawberry extracts are a source of bioavailable active compounds (phenolic components, coumarins, ascorbic acid, micro- and macronutrients) which, due to their plant nature, have a mild effect on the body, but do not cause side effects. Raspberry leaf and twig extract is an unconventional raw material and has not yet been used in beverage production.
3. The proposed new drink: "With the taste of honey". As an unconventional raw material, which is used to prepare a drink extract from twigs and leaves of raspberry, which is characterized by a high content of biologically active substances.
4. The optimal dose of making the extract of raspberry leaf powder into the syrup for mixing is not more than 3,0 cm^3 of 1% solution of grass.

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Some aspects of using the nanotechnology in food industry

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Abstract

Introduction. The article presents data from a literature review of the modern areas of nanotechnology application in food industry, their properties, interaction with biopolymers in food products.

Results and discussion. TiO_2, ZnO, and SiO_2 are the most common nanoparticles used in the preparation of food products or food-related ingredients. The food additive E551 (dioxide silica SiO_2) is mainly used as an anti-caking agent to improve the flowability of powdered or granular products and thus prevents the formation of lumps. At present, nanosized SiO_2 is one of the most common nanoadditives in various branches of the food industry. Scientific studies show that silica, due to its structural features and large surface area, has high adsorption properties with respect to water, proteins, exo- and endotoxins, and pathogenic microorganisms.

Numerous studies confirm the possibility of effective modification of the gum's rheological characteristics during their joint use with silica as a part of functional-technological compositions.

It was established by an experimental method that the addition of SiO_2 to the hydrated soy proteins and protein preparations containing collagen led to a densification of the mixture, modifying their rheological and functional properties.

Conducted scientific studies of the use of nanocomposites in the technology of meat-containing culinary semi-finished products confirm the effectiveness of the use of finely divided silica as a texture-forming additive.

If there are nanocomposites in the food product according to the European legislation, the application of the term "nano" should be applied to the label only if about 50% of the particles have a size in the range of 1–100 nm.

Conclusion. Nanoparticles directly affect the absorption and assimilation of nutrients due to physico-chemical modifications that occur during the interaction of food components with nanoparticles.

Nanotechnology is the technology of directional manipulation of material objects having molecular sizes in the range of 1–100 nm [1]. This is one of the most promising technologies for improving the food industry. The range and direction of nanotechnology application is determined by the functionality of nanoparticles. Nanocomponents can affect the bioavailability and nutritional value of foods, as well as their functionality [2]. It was found that the biological properties (including toxicological) of nanomaterials are largely dependent on their physicochemical properties [3]. Nanomaterials exhibit fundamentally new useful properties that are absent in substances represented by continuous phases or macroscopic dispersion. One of the main reasons for the appearance of such properties is an increase in surface area, which leads to a multiple enhancement of processes due to surface (interphase) interactions. The result, characteristic of nanomaterials, is a significant increase in interactions with other materials and biological objects. [1].

The main interactions between nanoparticles and food compounds and their direction increase food safety, extend shelf life, improve taste and nutrient intake, make it possible to detect the presence of pathogenic / toxic substances, pesticides, change the functional properties of products according to the scheme shown in Figure 1 [4].

An analysis of recent scientific developments and publications indicates the promise of using finely dispersed solid nanoparticles in food products, which are characterized by limited selective wetting, and therefore are able to be at the phase boundary. Such emulsions were given the special name “Pickering emulsions”, the advantages of which are higher stability, the ability to create highly concentrated systems, resistance to pH changes, low cost and environmental friendliness [5].

It can be argued that nanoparticles directly affect the absorption and assimilation of nutrients due to physico-chemical modifications that occur during the interaction of food components with nanoparticles [6]. The properties of nanoparticles also increase their attractiveness in terms of improving the absorption and bioavailability of additional nutrients, such as vitamins and minerals. Most studies focus on the use of nanotechnology in regulating the basic properties of packaging and food processing. [7].

According to the List of Consumer Products Based on Nanotechnology (CPI) created by the Woodrow Wilson International Centre for Scientists and the Nanotechnology Formation Project, commercial food products or food-related ingredients that include nanoparticles, TiO_2, ZnO and SiO_2 are the most popular [8]. These nanocomponents can be directly used in food products as additives or in the manufacture of packaging for various applications [9, 10]. TiO_2 nanoparticles (in the EU food industry additive with code E171) are used as white pigment [11], Ag nanoparticles (in the EU food industry additive with code E174) are used in food packaging as an antimicrobial agent, due to their antimicrobial activity against a wide range of microorganisms [12]. ZnO nanoparticles are used as a food additive or in the manufacture of packaging because of their significant antibacterial ability, especially against gram-positive bacteria [9, 13]. An important aspect for the use of ZnO nanoparticles in the food industry is that they enrich the product with Zn molecules, one of the most important microelements for humans [10].

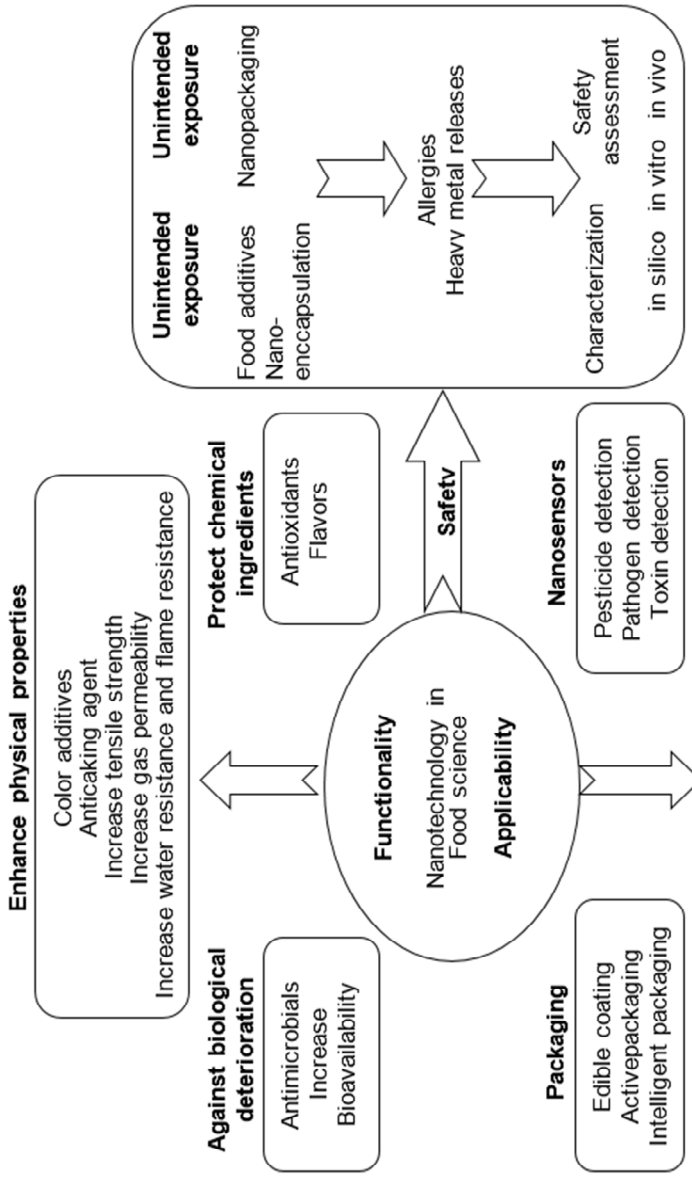

Figure 1. Main aspects development of nanotechnology in the food industry and the characteristic of functionality, advantages of use and safety [4]

The use of organic nanoparticles in the food industry is due to their functionality, which is to improve the basic properties of products [14]. Organic nanocomposites mainly consist of a combination of organic molecules of lipids, proteins and polysaccharides. These nanoparticles can provide encapsulation, transportation and release of food additives or active ingredients in the form of micelles or liposomes, increase the solubility of certain compounds, stabilize flavorings and / or dyes, which prevents the degradation of the basic properties of the product or additive during production and storage [15].

European law No. 1169/2011 stipulated that the term "nano" should be applied to the product label if about 50 % of the particles have a size in the range of 1–100 nm. Today, for food products in the nanoforms, only calcium carbonate (E170) and vegetable carbohydrate (E153) are allowed. Other potential nano-ingredients based on titanium dioxide (E171), iron hydroxide (E172), silver (E174), gold (E175), silicon dioxide (E551), calcium silicate (E552), magnesium silicate (E553a) and talc (E553b) are under study [15].

Amorphous silicon dioxide (SiO_2) obtained by aerosol or sol-gel methods, registered and approved in the EU and the USA as a food additive E551; It is mainly used as an anti-caking agent to improve the flowability of powdered or granular products and thus prevents the formation of lumps. [16, 17]. Synthetic amorphous silica is an anti-foaming agent during the production process, a means for lighting / purification of juices, oils, in brewing and as a carrier of flavouring / aromatic compounds of food products [18, 19]. SiO_2 is allowed to be used in an amount of up to 2 wt.% as a direct additive in food products [20]. With the development of nanotechnology, the particle size of food additives has reached the nanoscale. Currently, nanosized SiO_2 is one of the most common nanoparticles (NP) in various food industries. [21]. On its basis medical preparations are made adsorption action, carriers of biologically active substances, used as a thickener for liquid dispersion medium [22, 23]. Scientific studies show that silica, due to the structural features and large surface area (200 ... 400 m^2/g), has high adsorption properties with respect to water, proteins, exo- and endotoxins, pathogenic microorganisms. The latter should prevent or inhibit the growth of bacteria in foods [23, 24]. Its properties lead to an increase in the use of anthropogenic silica nanoparticles in various environments of the agro-industrial and food sectors that affect humans and the environment [25].

In a number of experimental and theoretical studies, the interaction of polymer chains with colloidal particles was studied [26], however, the nature of the interactions, the molecular structures formed and their influence on the main characteristics differ significantly for nanoparticles and depending on the nature of the interaction between the polymer chain and the particle surface affects the properties of the material. The formation of deformed secondary structures in solution through the interaction between their components changes the size of the base "fraction" and at a sufficiently high concentration of particles can form a spatial network [27].

In aqueous solutions, nanoparticles and polymeric compounds interacting with each other can affect the properties of the products and materials for which they are intended. The formation of nano- and microstructures in the middle of the dispersion causes complicated rheological changes, which include an increase or decrease in viscosity, as well as gel formation. The study of the properties of biopolymers, nanocomposites and their mixtures with controlled optical, electrical, mechanical properties is of considerable interest for use in materials science, wastewater treatment and industrial separation processes, in biomedicine, biotechnology and food industry [27].

Previous studies of silica nanoparticles in polysaccharide solutions have established the formation of a gel mediated by silica nanoparticles [28]. In the work of Jordan R.M. etc. [27] the effect of silicon dioxide nanoparticles on the properties of two biopolymers with different

conformations in solution was investigated, namely xanthan gum and locust bean gum (LBG), which are often used in food and cosmetic industries as thickeners. When mixing, both biopolymers interact with the formation of thermal gels, which are used in drug delivery systems, the formation of structures of animal products. The addition of silicon dioxide nanoparticles to the solutions of these hydrocolloids, as well as their mixtures, causes a modification of the basic structural and mechanical properties, which is manifested in a change in rheology, an increase in viscosity and elasticity.

Solutions of xanthan gum, a polyelectrolyte with a semi-rigid rodsimilar molecular structure, with using silicon dioxide in the form of a nanocomposite showed insignificant changes in viscosity over the entire range of shear rate changes and an increase in viscosity modulus with an increase the amount of silicon dioxide due to the interaction of their particles with each other and the formation of a larger number of bound sites polymer gel. This information is confirmed in our research [29].

LBG is a non-ionic compound with spiral molecules, the solutions of which are characterized by a decrease in viscosity with an increase in shear rate as it approaches Newtonian fluids. When 1 % nanocomposite is added, we observed an increase viscosity and relaxation time. When 10 % silicon dioxide is added, a gel-sol transition and change the viscosity characteristics has occurred. This is explained by both interaction with nanocomposites and between hydrocolloid molecules, and it is also possible for the polysaccharide surface not to be completely saturated with polymer nanocomposite molecules, which led to the formation of bridges between the molecules and particle aggregation [28].

In studies [30], there is information that the addition of silica leads to an increase viscosity characteristics aqueous solutions of guar gum by an average of 25 %, and after heating by 75 % compared with a sample without silica. This can be explained by the formation of associations of intermolecular chains due to the introduction of silica, which leads to the formation of complex three-dimensional networks are destroyed even at low shear rates, but increase the structural viscosity of aqueous solutions.

The synergy effect from the interaction of standardized solutions modified potato starch, "Extra" starch and milk whey, when 0,3 % fumed silica is added to them, has led to an increase in the effective viscosity values, which are intensified after the heat treatment of potato starch solutions "Extra" by 2,8 times, modified starch by 4,5 times, and whey solutions by 27 %, which makes it possible to standardize the characteristics of meatminced emulsions with various recipes composition [31].

In mixed solutions of xanthan gum and LBG in a ratio of 1: 1, when added 1 % or 10 % dioxide silica, the elasticity of the gel changes. When the temperature changes in the range of 20-85 °C, solutions using a 10 % nanocomposite under conditions of constant deformation were characterized by the stability of the elastic module. This indicates the ability of the hydrocolloid structure associated with the nanocomposite to counteract the influence of heat treatment, which is showed in the preservation of its basic properties [28].

This confirms the possibility of effective modification of the rheological characteristics of gums when their used together with silica as part of functional-technological compositions.

It was established by an experimental method that the addition of SiO_2 to hydrated soy proteins led to compaction of the mixture, modifying their structural-mechanical and functional-technological properties. The pH value did not change. Based on the hypothesis about the ability of the food additives E551 to stabilize the protein-water system, the most interest is the change in the indicator of water binding capacity (WBC). The results of the studies, taking into account the rational WBC value, at the level of 85 % for cooked sausage technology, indicate that the addition of silica in an amount of 0,3 % increases the WBC

value by an average of 3,6±0,1 %. This confirms the hypothesis that peptides and proteins can attach to silicon nanoparticles. The highest growth of WBC was recorded for the isolate and concentrate, and for the protein decrease in the maximum degree of hydration was observed using a nanocomposite. The values of the emulsion stability (ES) and emulsifying ability (EA) indicators for the isolate and concentrate indicate an increase in these indicators in samples with silica by 6-9 %, respectively. For protein, contrariwise, when silica is added, the ES and EA values decrease, and the product exfoliates. This is due to the destruction of the protein: fat: water system, which is associated, in our opinion, with the specific chemical composition of this preparation. Protein is not a pure protein preparation and includes other types of thickeners that have a syneresis with respect to SiO_2 [31].

The introduction of a silica nanocomposite in an amount of 0,3 % to animal origin protein preparations containing collagen of increases the WBC value of the gel of the studied samples by an average of 3,2 ± 0,1 %. The results of studies WBC indicator of selected hydrated proteins after heat treatment indicate that the same amount of silica gives a more positive effect. On average, WBC indicator increases from 3 % to 8 %, which is almost double the average for hydrated protein without heat treatment [32].

An analysis of the results given in work [22] confirms the advisability of using the food additives E551 to improve the ES and EA indicator for compositions based on a mixture of animal and plant origin protein preparations with hydrocolloids, because we observed their increase by average on 3-5 % compared with prepared samples without making it. The advantages influence of the additive E551 on these indicators is to facilitate the formation of the so-called spatial structure, which is able to hold the fat globules in its structure.

The material [33] studied the change effective viscosity of minced meat for low-calorie minced meat semi-finished products using a texturizing silica additive in the form of a nanocomposite. The obtained data indicate that, when SiO_2 was added to the model minced meats, the effective viscosity increased by an average of 16,5 %. The combination of bamboo fiber with silica enhances the effectiveness of fiber for thickening minced meat in the range of 3-5 %. Through the influence that silica exerts on meat raw materials, the increase in viscosity was about 17 %, which indicates a significant effect of the nanocomposite on the structure formation of minced systems by interaction with meat proteins.

Conducted scientific studies [1] confirm the effectiveness of the use of highly dispersed silica as a texture-forming additive in the technology of meat-containing culinary semi-finished products. Adding it in the amount of 0,3 % significantly improved the effective viscosity, ductility, water-binding capacity of structured products, resulting in increased product yield and reduced cost. Silica stabilized carotene-containing protein-fat emulsions and contributed to a better combination of plant and meat components. The developed products had excellent organoleptic characteristics and high consumer value, since they were characterized by a balanced chemical composition, high content of dietary fiber and carotene.

For our research we used nanocomposites (Amorphous dioxide silica (Aerosil) E551) with a specific surface area S=232 m^2/g and a corresponding average radius primary nanoparticles of 5,88 nm and bulk $\rho_0 \approx 22$ г/см^3 [34, 35]. In appearance – it is a crumbly bluish-white powder or crumbly granules without taste and smell.

According to hygiene standards, amorphous dioxide silica is allowed as a food additive that prevents caking and clumping in spices and products tightly wrapped with foil, in an amount up to 30 g/kg; in dry powdered products, including sugar, in cheeses, sliced or grated, and analogues of cheeses, in salt and salt substitutes in an amount of up to 10 g/kg; in products in the form of tablets, in biologically active food additives, in sugar confectionery, except chocolate.

Most often, food emulsifier E551 silicon dioxide is used as a part of the following food groups:

- Spices, seasonings, various ready-to-eat and dried spices;
- Powdered food products such as sugar, salt or flour;
- Dairy products, usually cheeses;
- Sweets and confectionery products;
- Various types of snacks, usually chips, nuts, as well as crackers and most other beer snacks;
- Alcohol products.

Conclusion

These results show that an understanding the effect of polymeric materials in the form of nanoparticles on the properties of compounds used in the food industry is a prerequisite for ensuring the forecasting and regulation of basic properties and parameters. A more complete understanding the nature of nanostructures in food products will provide greater opportunities for the rational selection, modification and recycling of raw materials. Thus, the use of nanotechnology should contribute to further improving the quality and safety of food products.

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Rational modes of wool scouring

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Abstract

Introduction. Currently, synthetic detergents with a weakly alkaline pH are used for scouring wool. The combination of surfactant Sles 70 with an aprotic organic solvent with dimethylsulfoxide (DMSO) allows you to create a neutral detergent and needs to determine the rational modes of wool scouring. The purpose of our study was to find the rational parameters of scouring fine-wool hair.

Materials and methods. In Latin squares, an experiment was conducted to determine the effect of the concentration of Sles 70 in the scouring solution in the range of 0.1 to 3.1 g/dm^3, the concentration of DMSO 0.01 to 0.61 g/dm^3, the hydromodule 10 to 100, the temperature of 30–48 °C for cleaning fine-wool fibers while scouring the wool fiber with the specified combined detergent.

Results and discussion. In the investigated range of variation of factors, the influence of the hydromodule on the purification of wool and the extraction of extractive substances from the surface of the fiber into the waste solution was most pronounced.

Hydro module 40 and more allows you to clean the wool from grease and dirt. The temperature has a stable effect in the given range, so all the investigated values of temperature contribute to the removal of fatty contaminations of wool for this component of the detergent solution.

According to the hydromodule 70 and 100, as well as the concentration of 1% by weight Sles 70 – that is, for concentrations of surfactants above the critical concentration of micelles (CCM) – the fibers of wool are also cleared during scouring. It is logical to note that the concentrations of surfactants below the CCM have reduced the effectiveness of wool cleaning. The concentration of DMSO also had a slight effect on the wool treatment compared to the hydromodule.

Conclusions.The rational mode of single scouring of wool is the use of a hydromodule 40, a concentration of 1% by weight. Sles 70 and DMSO concentration to 0.61 g/dm^3 in the temperature range 30–48 °C. The quality of the scouring can be improved by increasing the disposable water dispenser or by scouring it with a minimum of water.

Introduction

Pre-treatment of wool involves cooking, scouring, and drying. Typing (shaking) wool is used to remove easily separated contaminants (straw, sand). However, the presence of fat [1, 2], which lubricates the hair fiber and protects the flea from rain and dust contamination, does not contribute to the removal of all mineral contaminants. Therefore, in the future, the wool is cleaned of dirt during scouring. The process of scouring involves treating wool with detergent solutions to remove organic and mineral contaminants [3].

During scouring the wool on the process of scouring the dirt is influenced by the following factors: nature of contaminants and fibers, detergent, the hardness of water, the presence of electrolytes, pH of the scouring solution, temperature, mechanical influence on the surface of the fiber [4–6].

Wool is a natural fiber of protein nature [7]. It is known that the wool thin fibrous fiber has two layers: a scaly upper layer, created by horny cells, and a scalp-like inner layer made up by spindle-shaped cells. The fiber of the wool is called keratin. Molecular weight of keratin 60,000–1,000,000 a.o. The most effective sorption ability of moisture among all known fibrous materials is wool. The wool fiber is pierced with microscopic pores, which in dry condition have a size of 0.3–0.6 nm, and after swelling in water 4–6 nm. In the swollen state, fibers of wool in diameter increase by 10 times than the length [8].

There are two main modifications of the wool protein: α- (native fibers of wool) and β-structure (wool fibers, steam-treated or hot water) [9]. For light industry, it is important to have a conformation of the permanently fixed structure of keratin, which is obtained by treating the stretched fiber with steam.

One of the main characteristics of the protein is its isoelectric point. Keratin wool for the fiber of different breeds of sheep has an isoelectric point in the acidic region of pH values 4.2–4.8 [8]. In acidic medium, the fiber of the wool is more stable to hydrolysis, although the high temperature and high concentration of acid in the solution cause the hydrolysis of peptide bonds, which leads to the destruction of the fiber. The wool is easier to hydrolyze in the alkaline medium than in acidic. The wool in 3 % hot solution of alkali is immediately hydrolyzed and dissolved. Soda and ammonia solutions destroy the fiber of wool less than alkalis. Disulphide and peptide bonds are degraded by the action of reducing agents and oxidants. During the action on hydrogen peroxide, disulfide bonds split off with sulfur deposition. At concentrations of up to 5 g/dm^3 of hydrogen peroxide and temperatures up to 60 °C, pigments are bleached and keratin is practically not damaged. Loss of moisture in wool leads to its ability to electrify. At a temperature of 110–115 °C the wool becomes fragile and markedly yellow. At temperatures above 150 °C begin the processes of thermal decay, which proceed more intensively at temperatures above 170 °C with the appearance of smell burned feathers [8].

The elemental layer of wool has the form (-NH-CO-CHR-)$_n$, and the surface is uneven and slippery. It is also known that fibers of wool have reactive groups. Therefore, especially wool and woolen fabrics are the most contaminated, compared with other natural fibers. The wool has hygroscopic properties and can hold up to 42 % water [10]. At a temperature of 20 °C and relative humidity of 65 %, the humidity of the wool fiber is within 15–17 % [8]. The electrokinetic potential of wool is 48 mV [10].

During the scouring of wool, along with the separation of fiber dirt, a reversible sorption process occurs, and the cationic surfactants are most actively sorted on the wool fiber [10].

For wool, the temperature above 60 °C lowers elasticity of fibers. Also, the high temperature raises soap hydrolysis [11].

For treatment and scouring of wool fibers, surfactants are used [12–15]. Sodium, potassium, and ammonia soaps are anionic surfactants that have sufficient scouring and emulsifying properties but are sensitive to the action of acids and salts of water hardness. Also, anion-active surfactants are sulfonates – salts of sulfonic acids RSO_3Na, – which are different in structure and which include sulfonol. Sulphonols are sodium alkylbenzenesulfonates $C_nH_{2n+1}C_6H_4SO_3Na$ (n=12÷18). Sulfonols are used as wetting agents and emulsifiers of dyes during dyeing of fabrics and as detergents that exhibit good scouring ability [8].

Anionic detergent is sodium laureth sulfate (Sles 70), solutions up to 3% of which have a pH of 6.5–9.5. Sles 70 is the main ingredient in the hair shampoo formula.

Non-ionic surfactants do not dissociate in aqueous solutions. Products of condensation of higher alcohols with ethylene oxide are nonionic surfactants and include sintanols. Synthanol DS-10 is a mixture of products with the general formula $C_nH_{2n+1}O(C_2H_4O)_mH$ (n=10÷18, m=8÷10). Sintanol DS-10 is used in bleaching, dyeing of fibers and fur. Also, sintanol DS-10 has good emulsifying, dispersing and scouring properties.

Dimethylsulfoxide C_2H_6OS (DMSO) is an aprotic hygroscopic solvent, is soluble in water, ethanol, diethyl ether, chloroform, benzene. Looks like an oily liquid without odor. Thanks to the solvation of many organic and inorganic compounds widely used in cosmetics and medicines.

To remove fat from wool fiber use emulsion solvent, which to 90 % contains an organic solvent (including gasoline), up to 50 % aqueous sulfuric acid solution and an emulsifier (monoethanolamide) [UA 34016 A, 15.02.2001].

When scouring the wool fiber, a composition of synthesized surfactants, which includes anionic, nonionic surfactants and an organic solvent, is used. To remove contaminants and wool grease, a surfactant composition with a predominant anionic substance content (sodium dodecyl sulfate to 50 %) and nonionic substances (sintanol DS-10 and ricinose 80) and solvent (DMSO up to 10 %) are used [UA 32398 U, 12.05.2008]. Use composition of surfactants containing up to 55 % nonionic surfactants (ricinox 80), as well as anionic (sulfonol) and least nonionic surfactant (sintanol DS-10) [UA 32960 U, 10.06.2008]. The effective effect is the composition "Sulpsid-MPSH", which includes up to 65 % of nonionic surfactants (sintanol DS-10), as well as anionic (sulfonol) and up to 10 % DMSO [UA 57000 U, 10.02.2011].

Therefore, nowadays for scouring wool synthetic detergents with low alkaline pH are used [16, 17]. The search for effective detergents with neutral or slightly acid pH continues. The scientific and innovative combination surfactants based on Sles 70 with aprotic organic solvent DMSO will allow you to create a neutral detergent and will need to determine the rational modes of wool scouring.

The purpose of our study was to find the rational parameters of scouring fine-wool hair.

Materials and methods

Materials

The scouring of wool was studied with a combined detergent containing Sles 70 and DMSO. The selected kpmponents are chosen because the first one is a surfactant and the second one is the solvent of most organic substances. Solutions up to 3 % Sles 70 have a pH of 6.5–9.5. The critical concentration of micelles (CCM) for Sles 70 at 20 °C is 0.55 g/dm^3 [18].

Scouring solution preparation

The scouring solution was prepared by dissolving an anionic detergent sodium laureth sulfate (Sles 70), replacing the classical alkaline solution with a solution with a neutral pH of the medium. The influence of the Sles 70 concentration in the scouring solution in the range of 0.1–3.1 g/dm^3, the concentration of DMSO 0.01–0.61 g/dm^3, the hydromodule 10–100, and the temperature of 30–48 °C for removal from the sheep wool was determined extractives in a scouring solution.

Experiment planning

To find rational wool scouring options, the mathematical planning of the experiment in Latin squares was used. This experiment plan declares the absence of inter-factor effects. This involves the choice of independent factors and the use of the regression equations of the response dependence on the change of factors to find the optimal value of the factor in the selected range of variation. Each experiment experiment performed in triple repetition. Among the factors that were poured into the wool cleaning during scouring, the concentration of Sles 70 and DMSO in the scouring solution, the hydrodilution unit (water ratio: dry wool), the temperature was investigated.

The plan of the incomplete factor experiment is presented in the table 1.

Table 1

Planning a partial quotient experiment by latin squares in physical quantities of factor levels

Experiment No.	Concentration Sles 70, g/dm^3	Concentration of DMCO, g/dm^3	Hydraulic module	Temperature, °C
1	0.1	0.61	40	42
2	3.1	0.41	10	48
3	2.1	0.01	70	36
4	1.1	0.21	100	30
5	3.1	0.61	100	36
6	0.1	0.01	10	30
7	1.1	0.41	70	42
8	2.1	0.21	40	48
9	2.1	0.41	40	30
10	1.1	0.61	70	48
11	0.1	0.21	10	36
12	3.1	0.01	100	42
13	1.1	0.01	10	42
14	3.1	0.21	40	36
15	2.1	0.61	100	48
16	0.1	0.41	70	30

In response to the change in factors, the refractive index of the waste water was used, the fat content in the misty wool, the surface tension of the detergent before scouring and in the spent scouring solution.

Results and discussion

The influence of the investigated factors on the residual content of fat on the fiber of wool, on the refractive index of the waste of detergent solutions is given in Table 2.

Table 2

Influence the change of the factors of the incomplete factor experiment on fat content on the fiber (residual) and the refractive index of the spent scouring Solutions

Experiment No.	Fat content on fiber, % wt	Refractive index of waste liquids, *n*
1	12.74	1.3334
2	10.31	1.3342
3	11.14	1.3336
4	10.23	1.3336
5	10.81	1.3338
6	16.02	1.3338
7	10.99	1.3336
8	11.73	1.3336
9	10.88	1.3338
10	10.26	1.3336
11	10.12	1.3338
12	11.19	1.3338
13	11.42	1.3340
14	10.95	1.3338
15	11.29	1.3338
16	11.14	1.3336

In the investigated range of variation of factors, the most significant influence of the hydromodule on the purification of wool and on the transfer of extractives from the surface of the wool fiber to the treated scouring solution was most pronounced.

The plane describing the influence of the hydrodynamic modulus and the temperature in the normalized values on the refractive index of the used cleaning solutions has the form:

$$n = 0{,}0016 \cdot g^2 - 0{,}0098 \cdot g + 0{,}00003 \cdot t + 2{,}6815,$$

where n – the refractive index of the used detergent solutions,
g – scouring water module,
t – scouring temperature.

On Figure 1 shows the plane of the refractive index of waste liquids, depending on the change in the parameters of the hydraulic module and the temperature in the normalized values.

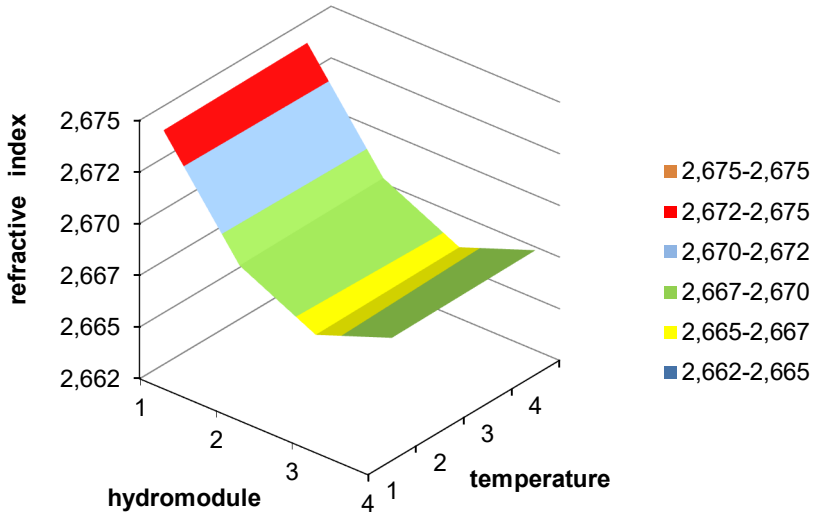

Figure 1. The response plane of the values of the refractive index of the spent scouring solution to the change of hydromodule and temperature taken in the normalized form

The smaller the hydromodule or the less the ratio of the scouring solution: dry wool, the more extractive substances pass into the waste solution.

The influence of temperature in the studied range is linear (see Figure 1). The content of the extracted substances dissolved in the spent scouring solution slightly increases with increasing temperature. This indicates that in the range of temperatures of 30–48 °C and for this component composition of the scouring solution all the pollutants of wool fibers are thoroughly dissolved in a scouring solution. Reducing the refractive index with the increase of the hydraulic module indicates dilution of contaminants in the scouring solution.

The plane describing the effect of the hydrodules and temperature in the normalized values on the residual fat content of the scoured wool fiber has the form:

$$f = -0{,}3956 \cdot g - 0{,}268 \cdot t + 24{,}313,$$

where f – the residual fat content of the scoured wool fiber,
g – scouring water module,
t – scouring temperature.

Determination of the fat content of the woolen fiber convinced that an increase in the hydrodules results in cleaner wool after scouring (Figure 2).

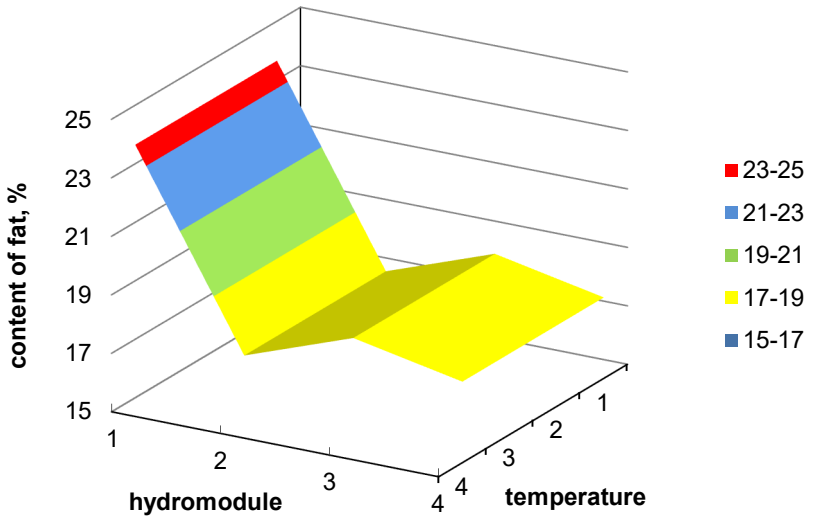

Figure 2. The response plane of the values of the residual fat content of the scoured wool fiber to the change of hydromodule and temperature taken in the normalized form

Hydromodule 40 and more allows you to clean the wool from grease and dirt. The temperature has a stable effect in the given range, so all the investigated values of temperature contribute to the removal of fatty contaminations of wool for this component of the detergent solution.

The plane describing the effect of the hydraulic module and the concentration of Sles 70 in the normalized values on the refractive index of the used cleaning solutions has the form:

$$n = 0{,}0016 \cdot g^2 - 0{,}0098 \cdot g + 0{,}00004 \cdot c^2 - 0{,}0001 \cdot c + 2{,}6815,$$

where n – the refractive index of the used detergent solutions,
g – scouring water module,
c – concentration of Sles 70 in a scouring solution.

The plane describing the effect of the hydrodules and the concentration of Sles 70 in the normalized values on the residual fat content of the scoured wool fiber has the form:

$$f = -0{,}3956 \cdot g + 0{,}335 \cdot c^2 - 2{,}129 \cdot c + 26{,}426,$$

where f – the residual fat content of the scoured wool fiber,
g – scouring water module,
c – concentration of Sles 70 in a scouring solution.

The concentration of Sles 70 in the scouring solution has even less effect on the scouring of contaminants in case of excess of its content in the solution of the amount of CCM (Figure 3 and Figure 4).

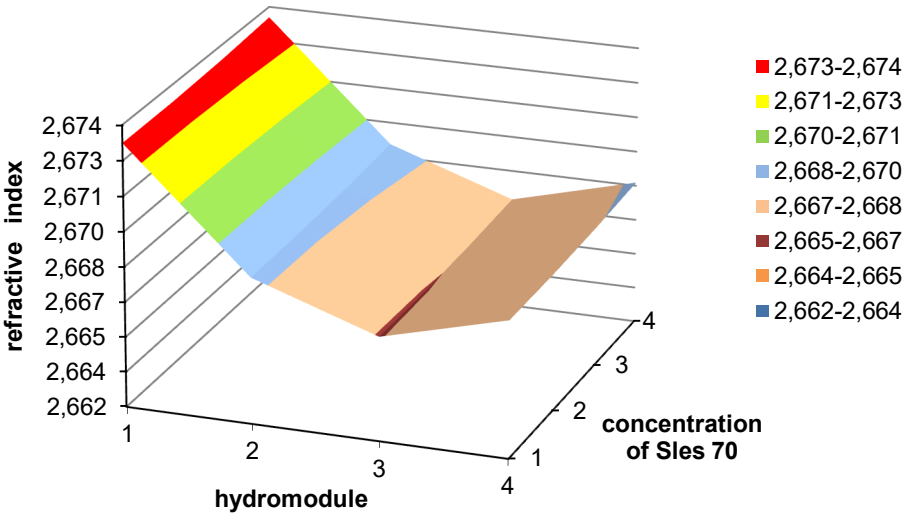

Figure 3. The response plane of the values of the refractive index of the spent scouring solution to the change of hydromodule and concentration of Sles 70 in a scouring solution taken in the normalized form

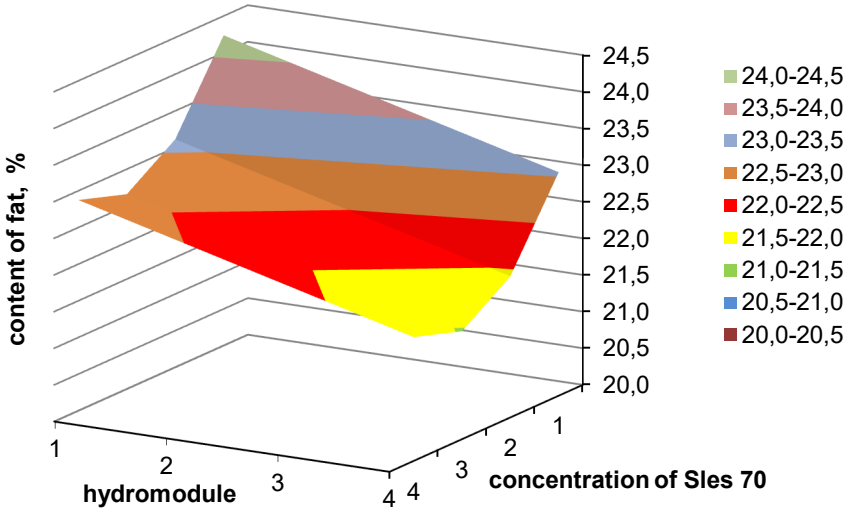

Figure 4. The response plane of the values of the residual fat content of the scoured wool fiber to the change of hydromodule and concentration of Sles 70 taken in the normalized form

The significant influence of the hydromodule on the scouring process overshadowed the effects of other investigated factors. Consequently, it is possible either to increase the disposable hydraulic unit or to scour it repeatedly for a minimum hydromodule. For multiple scouring, it is important to completely change the scouring solution in the mode of periodic successive scouring [UA 55426 U, 10.12.2010; UA 114837 C2, 10.08.2017].

For the hydromodule 70 and 100, as well as the concentration of 1% by weight Sles 70 (ie, for concentrations of surfactants above CCM), the wool fibers are best purified during scouring. It is logical to note that the concentrations of surfactants below the CCM have reduced the effectiveness of wool cleaning. This is evidenced by the high content of residual fat in the misty wool (see Figure 4). The concentration of DMSO also had a slight effect on the wool treatment compared to the hydromodule.

Conclusions

Currently, synthetic detergents with a low-fat pH are used for scouring wool. The search for effective detergents with neutral or slightly acid pH continues. Combining Sles 70 with an organic DMSO solvent can create a neutral detergent and needs to determine the rational modes of wool scouring.

In Latin squares, an experiment was conducted to determine the effect of the concentration of Sles 70 in the scouring solution in the range of 0.1 to 3.1 g/dm^3, the concentration of DMSO 0.01 to 0.61 g/dm^3, the hydromodule 10 to 100, the temperature of 30–48 °C for cleaning fine-wool fibers while scouring the wool fiber with the specified combined detergent.

In the investigated range of variation of factors, the most significant influence of the hydromodule on the purification of wool and on the transfer of extractives from the surface of the wool fiber to the treated scouring solution was most pronounced.

Hydromodule 40 and more allows you to clean the wool from grease and dirt. The temperature has a stable effect in the given range, so all the investigated values of temperature contribute to the removal of fatty contaminations of wool for this component of the detergent solution.

For the hydromodule 70 and 100, as well as the concentration of 1% by weight Sles 70 (ie, for concentrations of surfactants above CCM), the wool fibers are best purified during scouring. It is logical to note that the concentrations of surfactants below the CCM have reduced the effectiveness of wool cleaning. The concentration of DMSO also had a slight effect on the wool treatment compared to the hydromodule.

The rational mode of single scouring of wool is the use of a hydromodule 40, a concentration of 1 % by weight. Sles 70 and DMSO concentration to 0.61 g/dm^3 in the temperature range 30–48 °C. The quality of the scouring can be improved by increasing the disposable water dispenser or by scouring it with a minimum of water.

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Different methods of treatment of liquid systems and solutions: a review

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Abstract

Introduction. The purpose of this reseach is to investigate different methods of the treatment of the liquid systems and solutions for the change of the chemical and physical parameters and properties these liquid systems and solutions.

Materials and methods. Objects of research are different types of treatment and processing methods end modes of liquid water systems and solutions like as technological water for the application in food industry. Subjects of study are change of the physical and chemical parameters and properties of water systems and solutions. Scientific and research works, reviews, articles, monographs of different methods and processes of treatment water systems were analyzed.

Results and discussion. It is established that a great variety of methods of liquid systems and solutions treatment are widely used in different brunches of food industry. The application of actual type of processing depends from many factors.

The research studies confirmed the possibility to amplification technological processes by innovative reagentless methods of physical influences. Every of these methods, modes and approaches has its own objective problems, which need the modern original solutions,

Chemical methods of treatment give the possibility for disinfection, inactivating pathogenic organisms and these methods can be used with large volumes of water and water solutions

Biological methods of water, water systems and wastewater solutions treatment are an important and essential part of any wastewater processing.

The physical and chemical properties and parameters of water, and liquid mediums, such as: oxidation-reduction potential, pH value, dissolved oxygen and etc. may be changed by the physical methods of energy influence.

Conclusions. The application of different methods of treatment in combination could improve the water treatment process environmentally. One of original and new procedure and equipment that was used for improvement of water treatment process is the method of discrete-pulsed input of energy.

Introduction

At the present time one of the significant problems that are of attention to the scientific society is to extend original substandard goods and technologies that meet contemporary worldwide standards of quality and safety.

The availability of drinking water is limited, and it is shrinking worldwide. The world's 8.5 billion people will consume 6 trillion cubic meters (6000 km^3) of water per year [1].

Water is an exceptional, omnipresent substance that is a major component of all living things, which has anomalous in many of its physical and chemical parameters and properties. Pure water and liquid water solutions and systems are used for fabricating, processing, washing and cleaning, diluting, cooling, or transporting products. Worldwide, agriculture and power generation are the main consumers of this raw material [2].

The purpose of this research is to investigate different methods of the treatment of the liquid systems and solutions for the change of the chemical and physical parameters and properties these liquid systems and solutions.

Materials and methods

Materials

Objects of research are different types of treatment and processing methods end modes of liquid water systems and solutions like as technological water for the application in food industry.

Subjects of study are the changing of the physical and chemical parameters and properties of liquid water systems and solutions which can form hydrogen bonds and associates of different variety.

Pure water and associated liquid aqueous systems and solutions were used for investigations and analyzing the change of their physical and chemical parameters and properties during the treatment and processing by the different methods and technological modes.

Review methodology

Scientific and research works, articles, proceedings of the conferences, thesis of the conferences, monographs of different methods, modes, processes of liquid systems treatment and equipment for processing were analyzed.

General scientific methods, such as analysis, comparison, and synthesis were used for research investigation. Literature referenced in this review was obtained from searches from bibliographic information in database and logic programming (DBLP), ISI Proceedings, Journal STORage (JSTOR) Search, Medline, Scopus, CAB abstracts, CABI full text, EBSCOhost, Google Scholar, PubMed, Web of Science, Emerging Sources Citation Index Web of Science Core Collection, SciFinder, Universal Impact Factor, ScienceDirect, Science Research Portal, Ingenta, SciNet – Science Search, CiteSeer Publications Researchindex etc.

Results and discussion

Pure water and different liquid solutions and systems are plenty complicated associate systems, which are susceptible to the nominal quantity power influences.
In liquid solutions and pure water and in the aqueous solutions there is an unremitting three-dimensional grating of hydrogen bonds; it proves to be true many researches by the numerical mathematical experiments and by mathematical modelling methods [3, 4].

Water, liquid solutions and systems has been modeled by different ways:

- As a uncomplicated continuous medium for fast calculations of solvatation or dielectric properties;
- As simplified statistical mechanical sphere-like particles with hydrogen bonding arms;
- by using fixed charge or polarizable atomically detailed models in computer simulations and modeling;
- At the computationally exclusive – quantum mechanical level for insights into the nature of electronic structure and the bonding of the atoms [5].

A number of our grandest large-scale challenges – distributing clean water, producing cheap and clean energy, providing greater food security, green ways to produce modern chemicals, and curing diseases – depend on a better understanding of water at the molecular level [6].

Inescapability of investigate of the structural formation of liquid aqueous solutions and systems and also liquid binary systems is rooted by their exceptional properties, and also special importance in lifeless and alive environment, a science and the techniques, contemporary technologies and production. Interactions with water are a major driving force for bimolecular structure and function in living systems.

Water, liquid solutions and systems can proceed as a solvent, product, reactant, catalyst, chaperone, messenger, and controller.

Water has distinctive liquid and solid properties in one time:

- It is highly cohesive;
- It has volumetric anomalies – water's solid (ice) floats on its liquid;
- Pressure can melt the solid rather than freezing the liquid;
- Heating can shrink the liquid;
- It has more solid phases than other materials [7].

The special directionality of the hydrogen bonds is responsible for many of the anomalous water properties. The hydrogen bond H-bond is a strong bond which can formed between a polar hydrogen and another heavy atom, as a rule carbon, nitrogen, oxygen or sulfur in biological molecules [8, 9].

There are many methods of water treatment for changing chemical and physical properties and parameters. In recent years researches and technologists and engineers have turned their interest to employment of the innovative non-traditional technologies and methods in processing of the liquid mediums, solutions, systems, which consists of the water or water solutions.

Nanotechnology embraces grand guarantee in ensuring safe drinking water through designing innovative centralized and decentralized household-level water treatment systems such as such as nanoadsorbents, photocatalysts, microbial disinfectants and in membranes [10].

An explanation process of water treatment include flocculation, sedimentation and media filtration to remove colloidal and suspended solids, ion exchanging, carbon adsorption and membrane processes to remove dissolved solids; and at last stage a disinfection for microbial inactivation that often performed by chlorination, ozonation and ultraviolet radiation [11].

The processes implicated in treating water and liquid aqueous systems and solutions rationale may be chemical, biological, physical and different combination between of them.

The quantity and type of treatment and processing depends on the source of water, liquid aqueous systems and solutions the function for which the water is required.

The preference of which type of treatment or processing to employ from a great variety of available processes depends on the characteristics of the water, the kind of the water quality problems to be current, and the costs of different methods of treatments.

Chemical methods of treatment give the possibility for disinfection, inactivating pathogenic organisms and these methods can be used with large volumes of water and water solutions, Figure 1. Such methods described above can reduce the number of pathogens in water, but do not always eliminate them completely.

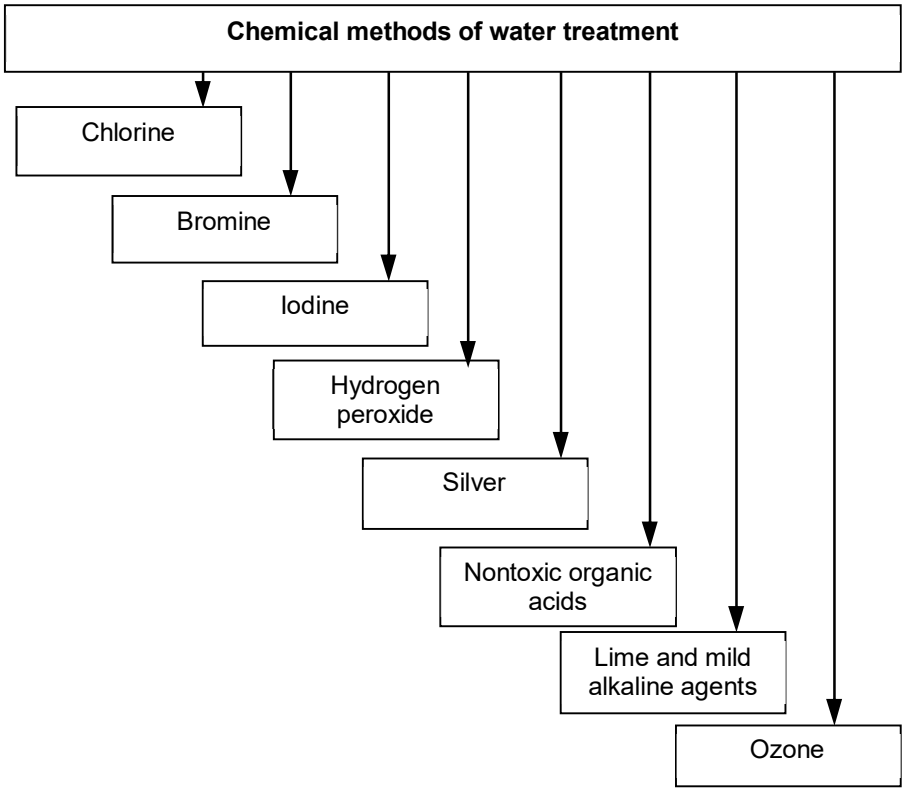

Figure 1. Some types of the chemical methods of water treatment

The main aim of the chemical methods of treatment water is to prevent pathogenic microorganisms causing the disease; to control unpleasant taste and appearance of particles; to remove the excessive color of water and turbidity; to extract the chemicals and dissolved minerals.

Chlorine is ordinary, inexpensive, but really toxic. Chlorine solutions lose strength while standing or when exposed to air or sunlight.

There are some types of chlorine used in water treatment. Some of them are:

– Chlorine gas;
– Calcium hypochlorite;
– Sodium hypochlorite;

Chlorine gas is greenish-yellow in color and heavier than air. Its high toxicity makes it an excellent disinfectant for water but also a danger to persons who handle it. Because of chemical changes that occur when it is introduced into water, chlorine gas is no more toxic to humans when used to treat drinking water than other forms of chlorine. Chlorine gas, which is really sold as an amber-colored compressed liquid, is the least expensive form of chlorine. Reactive chlorine species were main disinfectants at low current densities [12].

Calcium hypochlorite is manufactured from chlorine gas. It is best known as chlorine pellets and granules in water treatment. It is a white solid with a very pungent odor and it can create enough heat to explode. Calcium hypochlorite increases the pH of the water being treated [13].

Sodium hypochlorite is a chlorine-containing compound. It is a light yellow liquid that has a relatively short shelf life. It is the easiest to handle of all the types of chlorine. Sodium hypochlorite also increases the pH of the water being treated. A lower concentration of chlorine in this form is needed to treat water than with calcium hypochlorite or chlorine gas [14].

It does not decrease physical or chemical contamination. It does increase cholesterol formations, is a carcinogen, and causes heart infection. Besides disinfection of drinking water using chlorine can lead to the formation of genotoxic by-products when chlorine reacts with natural organic matter. Additionally, high dose chlorination of raw water induced genotoxicity [15].

The coagulant and chlorine consumption were also compared in the presence and absence of pre-sedimentation basin during non-flood condition. The results of investigations showed that in non-flood situation and using from pre-sedimentation tank didn't play significant role in decreasing the turbidity and coagulant consumption increased compared to none use of pre-sedimentation tank [16].

Bromine is used for water treatment, it is an oxidizing agent, and all form anions by accepting an electron, it has no smell and flavor as bad and doesn't kill microorganisms extremely well [17].

Bromine shows a very high reactivity toward phenolic groups, amines and sulfamides, and S-containing compounds, and high reactivity of bromine with inorganic compounds (NH_3 , I^- , SO_3^{2-}, NO_2^- , CN^- , etc) [18].

Model calculations show that depending on the bromide concentration and the pH, the high reactivity of bromine may outweigh the reactions of chlorine during chlorination of bromide containing waters [19].

Iodine is not useful, toxic but used for water treatment. Iodine is ineffective for treatment of water infected with parasitic worm eggs and larvae and doesn't eliminate or neutralize farming and manufacturing chemicals, or heavy metals from water and water solutions. This halogen can act in response with assured contaminants causing residual chemicals or byproducts in drinking water after treatment is complete and its efficiency depends on the temperature, the lower the temperature the slower disperses iodine [20].

Hydrogen peroxide exterminates microorganisms with oxygen, is chemically through and is very toxic. This method used in emergencies. When hydrogen peroxide is put in to water a great quantity of dissolved oxygen is released and an influential oxidizing effect takes place [21].

Hydrogen peroxide oxidizes the iron, manganese and sulphur odours to a solid form that the catalytic carbon can remove. For a lot of appliances no contact reservoir is necessary, and the hydrogen peroxide is successfully indifferent by the catalytic carbon medium [22].

Silver is a valuable antiseptic but accumulative toxins which concentrates and doesn't evaporate.

Nontoxic organic acids should be applied with carefulness no supplementary than in large water plants.

Lime and mild alkaline agents should also be applied with carefulness just by big water plants, or only for laundry. Lime has more than a few recompenses, they are:

– To control of the potential of hydrogen;
– To neutralize of acidic waste water:
– To decrease in the concentration of oxidizing organic impurities;
– The clarification,
– The precipitation of dissolved impurities as well as flocculation and coagulation of colloidal particles.

There are two way of the using lime for water treatment. The first way is the using of quicklime and slaked lime. At the present time the second way is the most widely used lime product in water treatment is calcium hydroxide ($Ca(OH)_2$), with a purity of more than 90%. The impact parameters which influence chemicals of emerging concern removal efficiencies of advanced water treatment technologies concern: chemicals of emerging concern characteristics; water matrix characteristics; treatment process conditions [23].

Neutralizing chemicals react with the unnecessary chemicals and produce outgases and sediment, but levels of need differ.

Coagulation-flocculation adds chemicals which lump together suspended particles for filtration or separation.

Ion exchange exchanges sodium from salt for calcium or magnesium, using either glauconite (greensand), precipitated artificial organic resins, or gel zeolite, thus softening the water. Minerals, metals, chemicals or odors are not affected, and the water is salty to drink.

Ozone can totally replace chlorine, chloramine or chlorine dioxide in the preoxidation and mainoxidation stages [24]. Ozone is an unstable gas comprising of three oxygen atoms, the gas will readily degrade back to oxygen, and during this transition a free oxygen atom, or free radical form.

The free oxygen radical is highly reactive and short lived, under normal conditions it will only survive for milliseconds. Ozone is effect over a wide pH range and rapidly reacts with bacteria, viruses, and protozoans and has stronger germicidal properties then chlorination.

Has a very strong oxidizing power with a short reaction time [25]. Ozone can eliminate a wide variety of inorganic, organic and microbiological problems and taste and odor problems.

Consequential from the enhanced microflocculation effect of ozone the filtration rates can be increased, smaller filtration beds used and even the chemical consumption lowered [26]. For the reason that of the higher oxidation potential of ozone it is also possible to reduce contact times, unless of course it becomes desirable to enhance the biological effect on granular activated carbon [27]. This method is very popular today.

Biological methods of water, water systems and wastewater solutions treatment are an important and essential part of any wastewater processing. Biological methods (Figure 2) of water treatment and processing are including: aerobic and anaerobic activated sludge processes, aerated lagoons, biofiltration.

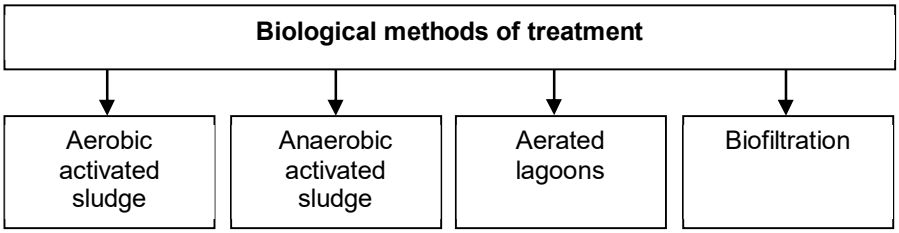

Figure 2. Some types of the Biological methods of water treatment

Biological treatment using aerobic activated sludge process has been in practice for well over a century. In general wastewater after primary treatment that is suspended impurities removal is treated in an activated sludge process based biological treatment system comprising aeration tank followed by secondary clarifier. The aeration tank is a completely mixed or a plug flow bioreactor where specific concentration of biomass is maintained along with sufficient dissolved oxygen concentration 2 mg/l to effect biodegradation of soluble organic impurities measured as biochemical oxygen demand or chemical oxygen demand [28].

Activated sludge systems, which are pure cultures and microbial mixed of the cultures, have been extensively studied, resulting in the deep understanding of the kinetics of the main and key heterotrophic and autotrophic biological processes, which sets the basis for the development of mechanistic models. A distinctive activated sludge wastewater treatment typically consists of a set of activated sludge tanks, sedimentation tanks; various recycle flows, and aeration systems of different types [29].

To model the biological wastewater treatment process, a high number of state variables and process descriptions, mostly based on Monod type kinetics, was used and combined in modeling structures [30].

Anaerobic activated sludge processes when the final products of organic assimilation in anaerobic treatment are methane and carbon dioxide gas and biomass.

Nowadays in wastewater treatment processes, physical and biochemical procedures are applied in order to decrease the organic matter levels, eliminate pathogenic organisms and improve water quality, so that water can be reused or released into the environment with minimal consequences.

Wastewater treatment processes carried out on aerated lagoons are widely used due to their relative low cost and maintenance requirements, minimum production of sludge and integration in the environment.

The system is based on the degradation and uptake of organic matter by a microbial community under toxic conditions [31].

A good understanding of the hydraulic performance of aerated lagoons is required for their design and operation. As a result a widespread numerical procedure has been developed for the three-dimensional computational modeling of the flow in large lagoons including high speed floating mechanical surface aerators [32].

At the present time biofiltration is widely used in drinking water treatment and in technological processes at plants as a supplement or enhancement of the conventional treatment [33]. Biofilters have dual utilities: the first is reducing the turbidity and pathogen particles like the conventional filters, and the other is removing the biodegradable organic matter and other bioavailable materials through the microbial metabolism of the biofilm attached to the media [34].

The second utility currently draws more attention because the micro-pollution of source water with biodegradable organic matter has become a common problem in many countries, especially in economically booming ones [35].

Biofiltration processes have developed over time, with careful filter media selection, nutrient and trace metal supplementation, oxidant amendment, and bioaugmentation of key microorganisms, to achieve improvements in water quality.

Biofiltration is on the precipice of a revolution that aims to customize the microbial community for targeted functional outcomes which might be to enhance or introduce target functional activity for contaminant removal, to keep away from hydraulic challenges, or to silhouette beneficially the downstream microbial community [36].

The physical and chemical properties and parameters of water, and liquid mediums, such as: oxidation-reduction potential, pH value, dissolved oxygen and etc. may be changed by the physical methods of energy influence.

Non-reagent methods and modes of water processing and liquid water binary systems treatment are shown on Figure 3.

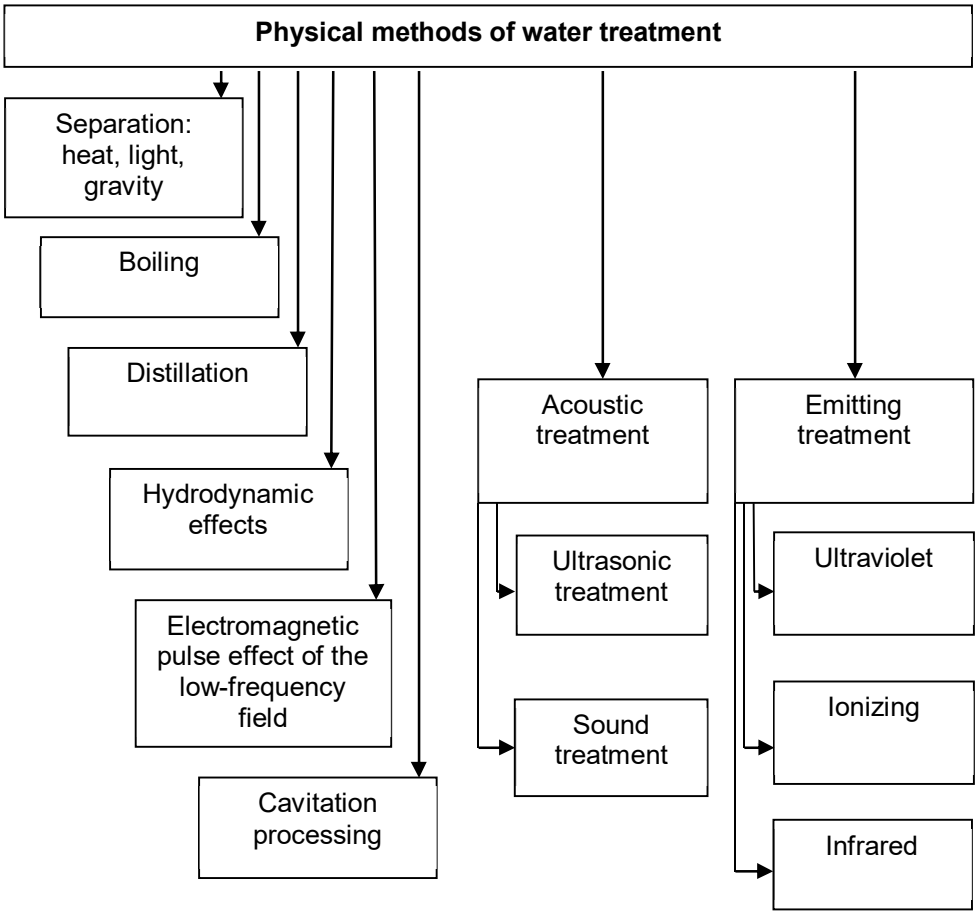

Figure 3. Some types of the physical methods of water treatment

They include: separation: heat, light, gravity; boiling; distillation; hydrodynamic effects; the electromagnetic pulse effect of the low-frequency field; cavitation processing; acoustic treatment: ultrasonic treatment, sound treatment; emitting treatment: ultraviolet, ionizing, infrared.

Separation: heat, light, gravity gravitationally settles heavy suspended material. Removes suspended particles from water to improve its appearance. As a result of such treatment, water turbidity and color index are reduced.

The effectiveness of sedimentation may however, be increased by mixing certain chemicals with water, to form flocculent precipitates, which carries the suspended particles as it settles The finer particles in suspension, which may avoid settling in sedimentation basins even after using the chemical coagulation, may then be removed by filtering the water through filters [37].

Boiling kills 99.9% of all living things and vaporizes most chemicals. Minerals, metals, solids and the contamination from the cooking container become more concentrated [38].

Distillation boils and recompenses the water, but many chemicals vaporize and reconvene in concentration in the output water.

Boiling and distillation are very expensive and with high energy consumption methods of water treatment.

A great number of alternative methods are commercially available for the elimination of microbiological pollutants and several chemical contaminants from water sources.

Hydrodynamic effects occur at water and water binary systems and different water mixtures and solutions treatment by physical and mechanical methods or so-called non reagent (reagentless).

The method of discrete-pulsed input of energy (DPIE) is one of physical methods of treatment with many hydrodynamic effects, such as power of pressure of shift, cavitations, the effect of explosive boiling, collective effects in assembly of vials, crossness of an interphase surface in gas-liquid bubbly medium, action of hydrodynamic oscillations, alternating impulses of pressure, effects which associated with acceleration of movement of a continuous phase.

The major effects of the discrete-pulsed input of energy are related with increase of velocity of association of a continuous phase of medium.

The method of DPIE can influence on structural and energy transformation in multifarious liquid mediums on micro- and nano- level and gives opportunity to begin physical and chemical alteration in these mediums [39].

The fundamental nature of a DPIE method consists in that preliminary permanently entered and any rank the energy distributed in working volume to accumulate in locally disconnected discrete points of system and further pulse to realise for achievement of necessary physical effects: forcing and dumping of pressure, adiabatic boiling, hydraulic blow, shock waves of pressure or depression, pressure of shift, local turbulence, cavitation and many other effects [40].

Three-dimensional and period concentration of energy gives the possibility to receive the big capacity of pulsation power accomplishment, to release internal energy of substance, to create active energetic processes which take place at microlevel and also at nanolevel.

The development of different microliquid devices for some last decades has caused growth of interest to microscale streams. Rotary pulse apparatus are characterised by small enough sizes of width of channels which gives the chance to consider them as microchannels with effects of slippage a stream on walls.

A number of heat and mass technological processes (structuring, crushing, dispersion, emulsification, homogenization, mixing, etc.) are spend in rotary pulse apparatus of cylindrical type which realise principles of discrete-pulsed input of energy.

Investigating of new methods, apparatus and industrial technologies are concentrating on raise of an overall presentation of procedure and an increase of processes in environments which involves complex researches on learning of hydrodynamic conditions, modelling of processes in new devices.

In recent times there has been considerable investigation of the electromagnetic pulse effect of the low-frequency field on water or on the behaviour of aqueous solutions. The physical and chemical properties and parameters of water, such as: oxidation-reduction potential, potential of hydrogen, dissolved oxygen and atc. may be tainted by the magnetic and electromagnetic fields. These changes depend from the field intensity and frequency. Even though intensive research, the mechanisms by which electromagnetic fields act on water are still a controversial issue [41]. Extremely low frequency electromagnetic fields have significant and lasting effects on liquid water [42].

The majority of theories explain effect of magnetic processing of water magnetic field achievement on there is at water ions of salts which are exposed to polarisation and deformation [43]. As main and explanation parameters of devices for processing of water by a magnetic field intensity of a magnetic field, time of stay of water provide in an active zone or sector of a magnetic field, frequency velocity and periodicity of power influence of a field on water, speed of a stream of water in the device [44].

Today the cavitation processing is one of the innovate technologies that was used for improvement of water treatment process. By definition cavitation consists in formation of ruptures of sites of liquid small vials, under the influence of the intelligent changes of pressure caused by movement of a liquid.

The cavitation is the experience of the formation, growth and collapse of microbubbles or cavities occurring in extremely small interval of time milliseconds in a liquid [45].

The cavitation can be used as the working instrument for the organisation of different technological processes, for example for: clarifications and processing's of surfaces, hashing of multiphase streams: a liquid - a liquid, gas - a liquid, firm particles - a liquid etc., activation of chemical reactions, structuring and is finishing, in technologies of clarification and water disinfecting. In the conditions of cavitation hydroxyl (OH^-) and hydrogen (H^+) radicals would be formed by thermal dissociation of water and oxygen [46].

At the present time the numerous applications of acoustic treatment: ultrasonic treatment and sound treatment, the advance is employed in the field of water treatment.

Among available technologies, ultrasound technology has a significant potential to produce good-quality, healthful, delicious, and affordable convenience food products and different drinks [47]. The numerous applications of ultrasound, the come within reach of are used in the field of water treatment for different brunches of industries and productions.

Ultrasonic treatment in a liquid leads to the acoustic cavitation phenomenon such as formation, growth, and collapse of bubbles – cavitation, accompanied by generation of local high temperature, pressure, and reactive radical species (OH, OOH) with thermal dissociation of water and oxygen [48].

Nowadays emitting treatment is very perspective method of the processing. There are many modes and different combinations of the emitting treatment for the water solutions processing for foodstuff production. This method includes: ultraviolet, ionizing, infrared emitting.

Conventionally, the ultraviolet spectrum is divided into three discrete sections: Ultraviolet A, with wavelength 320-400 nm; Ultraviolet B, with wavelength 280-320 nm; Ultraviolet C, with wavelength less than 280 nm [49].

Revelation to ultraviolet light can consequence in the construction of a range of photoproducts whose distribution and comparative yields depend on the wavelength and intensity of occurrence emission.

Infrared mode of treatment of water and water solutions used for micro-organism inactivation, disinfection also for structural transformation by the infrared radiation and emission.

But infrared laser water treatment apparatus is limited, on the other hand, by the energy consumption and expenditure required activating water properties and parameters [50].

The photocatalysis has immense potential as an unconventional or alternative water treatment and processing method outstanding to possibility to remove by-product precursors [51]. This process also ensures the public health safety of drinking water due to its ability to inactivate micro-organisms and to change physical and chemical parameters of water.

The photocatalytic procedures are divided into two processes: homogeneous photocatalytic oxidation, for example ultraviolet or hydrogen peroxide and heterogeneous photocatalytic oxidation, such as ultraviolet or semiconductor photocatalysis [52].

Further investigation is needed to better understanding of the change physical and chemical parameters of water systems and technological water solutions during treatment. It will give the possibilities to create and design new energy and power saving technologies, modes, equipment and apparatus of water treatment for foodstuff production.

Conclusions

As a result of research, it was found that the application of different methods of treatment in combination could improve the water treatment process more environmentally.

Every of these methods, modes and approaches has its own objective and intention problems and its own research area.

At the present time one of original and new procedure and equipment that was used for improvement of water treatment process is the method of discrete-pulsed input of energy.

There are many various parameters that can affect to application and efficiency of in discrete-pulsed input of energy on water treatment such as: power, frequency, velocities, constructive design of the working chamber and clearances, time of processing.

Experimental and theoretical studies have shown that the method of discrete-pulsed input of energy may be suitable for processing in food industry, where hydrodynamic effects are found to be an alternative to traditional methods of technological water and water solutions treatment.

The various parameters and effects could influence to the efficiency of the processing and can greatly reduce the duration of the process, reduce power and raw material consumption, increase capacity.

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Analysis of causes, circumstances and consequences of occupational traumatic injuries at the food beverage enterprises

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Abstract

Introduction. The purpose of the study is to determine the causes, consequences and circumstances of occupational injuries at the food beverage enterprises for the period from 2010 to 2018 in Ukraine.

Materials and methods. Applied statistical analysis of data on accidents occurring at food processing enterprises in the production of beverages for the period from 2010 to 2018 was applied during the study; principal component method. The work up of trends in the time series of industrial injuries is based on data from the State Statistics Service of Ukraine.

Results and discussion. In the food industry in the beverage production 221 workers were injured at the food factory, 35 of them died. Of these, 75.6% were male, 24.4% were 3 female which is 3 times less than male. It was found that organizational factors lead to 80% of industrial injuries, the most common organizational reasons were: violation of traffic safety rules (12.8%), violations of labor and industrial discipline (11.2%), shortcomings in training of safe work practices (9%), non-compliance with the requirements of labor safety instructions (8.2%) of the total number of injured workers in the food industry in the production of beverages; violation of safety requirements during the operation with the equipment, machines, mechanisms (7.4%), failure to fulfill official duties, lack of proper control by managers (5.4%).

Among the technical reasons, the dominant are the following: design defects, imperfections, insufficient reliability of means of industry, vehicles (5.4%); poor technical condition of industry facilities, buildings, structures, utilities, territory (3.6%); insufficiency of technological process, its non-compliance with safety requirements (2%). Psychophysiological causes of trauma are also considered.

Conclusion. Organizational factors lead to 80% of occupational injuries, of which more than 63% of all are for workers of 30 to 50 years of age. Basically, violations occur because of poor knowledge of security rules by workers.

Introduction

Labour safety have become important cornerstones of social development. Important question is an effectively manage of occupational safety problems.

Occupational injuries and diseases are costly for companies and for society as a whole [4, 28].

The continuing high frequency of the food industry occupational accidents calls for new approache for understand the underlying factors [12, 25].

A safe, healthy work environment is a crucial factor in a person's quality of life and it is a collective problem. The governments of the EU Member States and the US Government recognize the social and economic benefits of improving health and safety at work [5]. Reliable up-to-date statistical information is vital to setting policy goals and taking appropriate measures and preventative measures [1–2].

It is necessary to implement the selection and concentration by identifying the characteristics of high-risk groups necessary for an effective prevention against and reduction of occupational injuries, including fatal [19].

The purpose of the study is to determine and analyze the causes, consequences and circumstances of industrial injuries at the food beverage enterprises for the period from 2010 to 2018 in Ukraine.

Materials and methods

Materials

The work up of trends in the time series of occupational injuries is based on data from the State Statistics Service of Ukraine, taking into account Framework Directive 89/391/ EEC [16] on measures to improve occupational safety and health at work.

Occupational injury statistics are relevant for different countries of the world. Thus, the processing of European statistics on industrial accidents at work is based on the ESAW methodology (ESAW), the US Bureau of Labor Statistics [8] collects data on industrial injuries and diseases; occupational health and safety data are presented in the UK summary statistics [9].

An applied statistical analysis of accidents occurring at the food industry of Ukraine in the production of beverages for the period from 2010 to 2018 was applied during the study.

Methods

In the analysis of the statistical data of the causes, consequences and circumstances of industrial injuries in food industry in the production of beverages used: method of applied statistical analysis [17] of data on accidents to determine the general trends of injury in the industry; the principal component method [18] for determining the main causes of injury to industry employees.

Results and discussion

Statistics of accidents at the enterprises of the food industry of Ukraine, show that despite the general tendency of decrease of the number of accidents at the factories in

Ukraine, in the food industry, the level of industrial injury remains high. The analysis of the dynamics of industrial injury for the period from 2010 to 2018 showed that 221 workers were injured at food enterprises in the production of beverages (Figure 1) [2–3].

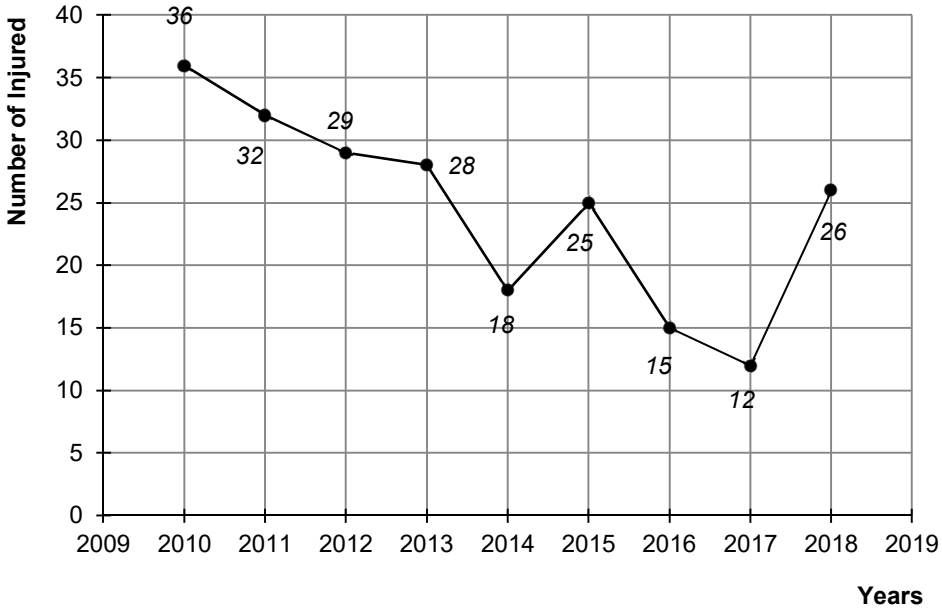

Figure 1. Dynamics of occupational injury at food processing enterprises in beverage production, 2010–2018

According to the results of the statistical analysis, 221 workers were injured at food processing enterprises in the beverage industry from 2010 to 2018. Of these, 75.6% were male and 24.4% were female, which is 3 times less than the level of injury for men (Figure 2).

According to the analysis of the industrial injury survey for the period 2008–2018, it was found that about 55% of accidents at the food industry in the production of beverages are related to the operation of the equipment, machines, mechanisms, vehicles.

Analysis of the dynamics of occupational injuries from 2010 to 2018 showed that during that time in the food industry in the beverage production 221 workers were injured at the food factory, 35 of them died. Of these, 75.6% were male, 24.4% were female which is 3 times less than male. It was found that organizational factors (Figure 3), lead to 80% of industrial injuries, the most common organizational reasons were: violation of traffic safety rules (12.8%), violations of labor and industrial discipline (11.2%), shortcomings in training of safe work practices (9%) , non-compliance with the requirements of labor safety instructions (8.2%) of the total number of injured workers in the food industry in the production of beverages; violation of safety requirements during the operation with the equipment, machines, mechanisms (7.4%), failure to fulfill official duties, lack of proper control by managers (5.4%).

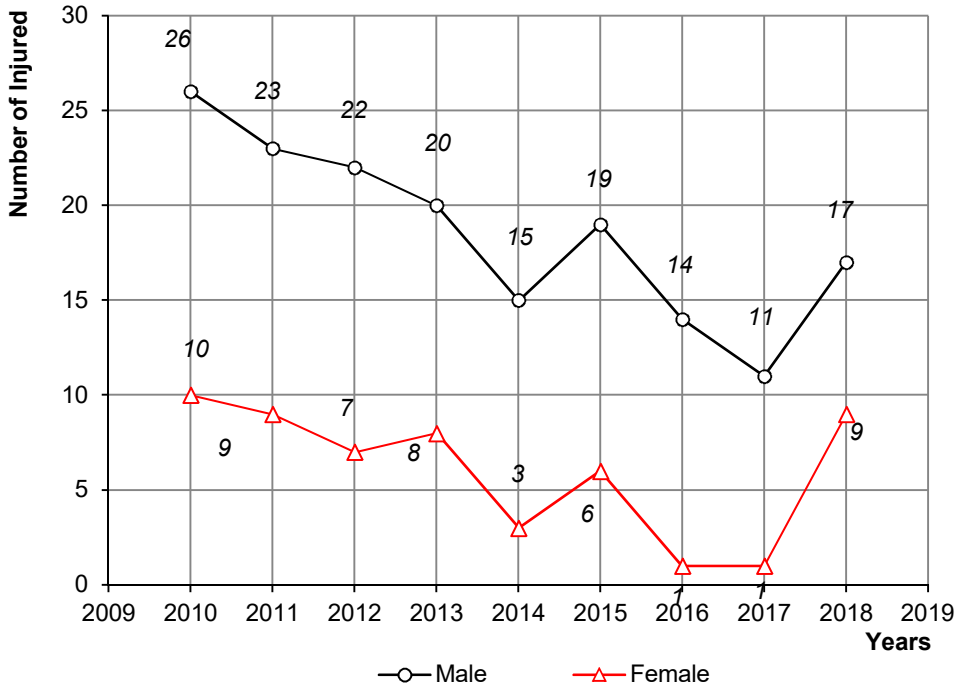

Figure 2. Dynamics of the numbers of injured male and female workers in the food industry in the production of beverages, 2010 – 2018

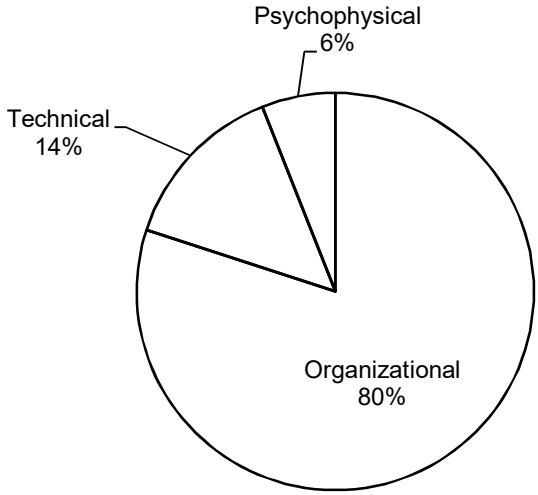

Figure 3. Dividion of the number of victims of occupational injuries by main causes at the food industry in the production of beverages, 2010 – 2018

World statistics confirmed that men and women faced different levels of risks in distinct work environments [27].

According to results, male workers have comprised a large proportion of occupational fatalities. A common explanation for men has been that men are overrepresented in more physically hazardous occupations. Yet another potential explanation is that prescribed gender roles and norms contribute to higher rates of male worker fatalities compared with female workers [23].

It was payed attention, that men may be at increased risk for occupational fatalities when compared to women in the same occupations, and advocate for investigating the role of gender for future research on injury and fatality discrepancies between male and female workers [23].

Among the technical reasons, the dominant are the following: design defects, imperfections, insufficient reliability of means of industry, vehicles (5.4%); poor technical condition of industry facilities, buildings, structures, utilities, territory (3.6%); insufficiency of technological process, its non-compliance with safety requirements (2%).

The most common psychophysiological reasons were: alcohol-related injuries (3.8%) and unlawful acts of others (1%), personal negligence of the victim (1%) of the total number of injured persons in the food industry.

The analysis of statistics shows that for the types of events that lead to accidents at the food industry, the major ones are the following: the car accidents both on public roads and on the territory of the enterprise (24.6%); the action of objects and parts that move, fly, rotate (12.4%); fall of the victim (9.2%), including from the height (4%); and falls, collapses, falls of objects, materials, rocks, soil, etc. (4.8%).

The influence of various factors (total work experience, specialty experience, age of the victims) on the magnitude of the frequency of injury was analyzed.

Of particular concern is the fact that more than 63% of all accidents occur to workers of 30 to 50 years of age. Most workers of this age have managed to change several jobs at different factories, over-confident and overestimating their own capabilities, which diminish attention and lead to violation of safety rules during the technological process, which eventually creats an emergency situation.

Some scientist pay attention that mechanical factors such as heavy lifting, psychosocial factors such as low control over work pace, and organizational factors such as safety climate are all associated with increased injury risk for young workers. Researchers and practitioners have to account for this complexity in the education, training and organization of work, and workplace health and safety culture [24].

A large part of the injuries happens to the workers with more than 20 years of experience and those with 1 to 5 years of professional experience. Both categories are characterized by an extremely negative factor with hyperbolization of one's own experience in dealing with standard situations [5]. Particular attention should be paid to these facts during the first meeting and repeated on the job briefings. In addition, it is necessary to improve the quality of the briefings themselves, to strengthen the control over the work of employees with little professional experience.

The fatal accidents have been analyzed separately. According to the results of the statistical analysis, 35 employees died at the food processing enterprises in the beverage production from 2010 to 2018.

The analysis showed that more than 30% of the employees who died at the food processing industry in the beverage production don’t go through training of the profession during which the accident occurred. In addition, no introductory instruction was conducted to the 12% of the victims. Knowledge testing for high-risk works has not been conducted for

more than half of the dead. These facts testify to the shortcomings in the professional training of industry workers and poor, formal training at food processing enterprises. According to the study, the victim violated labor law in 48% of accidents with fatal consequences, while the other in almost 52%. In more than half of the accidents, the ones who violated the rules were at different levels in the labor protection legislation. Therefore, there is a need to increase the accountability of managers at all levels in industry to prevent them from violating labor safety laws that lead to accidents.

Summarizing the above, it can be said that organizational and qualification factors in food processing companies lead to 80% of occupational injuries. Basically, these violations occur because of poor knowledge of security rules by workers. This problem is caused by the insufficiency of training, the formalism in the training and in the instruction of workers at the workplace, the little knowledge of labor protection requirements by workers.

For this reason, in order to prevent occupational injuries and increase the level of safety at food processing enterprises in the of beverage production to employers, it is necessary, first of all, to strengthen the control over the compliance with traffic rules by employees whose work is related to the transportation of food products; improve the quality of training and development of safety instructions; improve the effectiveness of training and validation of occupational safety knowledge of workers, including those employed in high-risk jobs; provide monitoring of production equipment, control systems, production process management, alarms and communications; to monitor compliance with the requirements of legislative and regulatory acts on labor protection by both employees and managers of structural units. The foresight research is considered to be an obligatory tool for successful scientific, technological and innovation policy [6, 7].

Despite the positive changes, Ukraine is still ahead of the developed countries in terms of the number of injured persons in production–10]. Among the main reasons are the general socio-economic situation in the country, lagging behind world trends and developments in the field of labor protection. The level of occupational injuries of the countries of Western and Eastern Europe of Japan, the USA, the United Kingdom is closely connected with more advanced technological processes, the equipment, and also the organization of production.

Pay attention on the conclusion [20] that personal perceptions of occupational risk are inaccurate, perhaps because workers are usually fully informed about work-related risks only after wage negotiations are concluded and a contract is signed.

The emphasis on the innovative dimensions of prevention activities, the intensive use of quality management tools, and the empowerment of workers are all factors contributing to reduce the number of injuries. By contrast, the implementation of flexible manufacturing processes is associated to higher accident rates [26].

Many industries are concerned about adopting an appropriate shift schedule for their workers. Interesting result show the research of impact on a group of production workers of changing from an 8-h to a 12-hr rotating schedule [29]. It was indicated a strong preference of the workers for the 12-h schedule with positive influences on the workers' subjective feeling toward health and social family life. That study also indicated that there was no significant change in the occupational injury rate [29].

Therefore, for the constant control and monitoring of the state of occupational safety, it is necessary to introduce modern information and analytical systems of occupational safety management, which should be organized taking into account the clear interaction of the head of the service (department) of occupational safety with the managers of all structural divisions of the food enterprise, for adequate and permanent management of taking into account all factors affecting the state of occupational safety and providing managers of structural units with an optimal set of measures to ensure safety at work [11–15].

Conclusion

The level of occupational injury remains high, for the period 2010–2018, 221 workers were injured, 35 of them died. The study found that organizational factors lead to 80% of occupational injury. More than 63% of all accidents happened to employees of 30 to 50 years of age. Most of the injuries happened to the workers with more than 20 years of experience and those with 1 to 5 years of professional experience. In more than half of the accidents, the ones who violated the rules were at different levels in the labor protection legislation. Particular attention should be paid to these facts during the first meeting and repeated on the job briefings. In addition, it is necessary to improve the quality of the briefings themselves, to strengthen the control over the work of employees with little professional experience. It is necessary to increase the responsibility of managers of all levels in industry in order to prevent them from violating the labor protection laws that lead to accidents.

The results of the studies can serve as a theoretical basis for the construction of a mathematical model of optimal planning of occupational safety at food industry in the production of beverages in order to significantly reduce the level of occupational injury.

Safety professionals and researchers can use the study findings to inform future intervention efforts in this industry [21].

The results of the study can also be of assistance for professionals involved in planning, implementing and controlling the national policy and/or regional policies on safety and health at work [22].

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Анотації

Харчові технології

Вплив додавання борошна пінхао і жому, утвореного після вилучення крохмалю, на рецептуру печива

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Вступ. Пінхао *(португальською – pinhão)* – плід Араукарії бразильської. Після процесу вилучення крохмалю з насіння пінхао утворені залишки, зазвичай, не використовуються, тому мета дослідження полягала в тому, щоб обґрунтувати використання цього побічного продукту як потенційного замінника пшеничного борошна у складі печива.

Матеріали і методи. Насіння пінхао закуплено у місцевих підприємств Понта-Гросса-PR (Бразилія). Після водного вилучення крохмалю, залишки, що утримуються в ситі, перемелювали для отримання борошна. Печиво було розроблено за симплекс-центроїдною експериментальною технологією, що передбачає використання пшеничного борошна, цільного борошна пінхао і залишкового (жомного) борошна після вилучення крохмалю пінхао.

Результати і обговорення. Борошно і печиво, виготовлене з *пінхао* та жому, і, відповідно, печиво на їх основі мали високий вміст клітковини. У пшеничному борошні був більший вміст білка (13,59±0,38%) і ліпідів (2,00 ± 0,02%), ніж у борошні *пінхао* і жомі. Зразки печива з пшеничним борошном і жомом або пінхао і жомом мали високий вміст ліпідів (18,44±0,32% та 18,82±0,09% відповідно). У печиві з додаванням жому спостерігалося зменшення видимого і питомого об'єму. Додавання борошна пінхао до печива забезпечувало більшу м'якість, на відміну від додавання жому. Відмінності спостерігалися в кольорі борошна, особливо в яскравості та хроматичності a*. Пшеничне борошно виявило меншу яскравість, можливо, завдяки підвищеному вмісту золи, що безпосередньо впливало на низьку яскравість печива з його додаванням. Крім ускладненого процесу тістоприготування, жомне борошно надавало печиву більшої твердості. Додавання трьох видів борошна в однаковій пропорції показало цікаві результати для застосування в печиві.

Висновки. І борошно пінхао, і жом, отриманий після вилучення крохмалю, є потенційними джерелами заміни пшеничного борошна, що дає змогу підвищувати цінність вихідної сировини та готових продуктів.

Ключові слова: *пінхао, араукарія, крохмаль, борошно, печиво.*

Умови вилучення токоферолів з дезодораційних дистилятів соняшникової олії

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Вступ. Дезодораційні дистиляти є відходами дезодорації жирів і природним джерелом токоферолів. У статті досліджено методи одержання природних антиоксидантів із соняшникових дезодораційних дистилятів.

Матеріали і методи. Для дослідження використані деодистиляти соняшникової олії. Неомилена фракція дезодораційного дистиляту була виділена після його омиленням. Кінетику окиснення соняшникової олії з антиоксидантами або без них досліджували волюметричним методом.

Результати і обговорення. Дезодораційний дистилят соняшникової олії збільшував період індукції окиснення соняшникової олії у 1,5 раза. Антиоксидантна активність одержаних концентратів підтверджена збільшенням індукційного періоду окиснення соняшникової олії майже втричі при додаванні у концентрації 50 мг/100 г. Таким чином, омилення дезодораційного дистиляту надає можливість одержати достатньо ефективний інгібітор окиснення.

Більш ефективним способом концентрування антиоксидантів із дезодораційного дистиляту була адсорбція токоферолів активованим вугіллям із гексанового розчину деодистиляту. З активованого вугілля токофероли запропоновано вилучати у вигляді розчину в м-ксилолі, після відгонки якого одержували концентрат токоферолів. Одержані концентрати збільшували період індукції окиснення соняшникової олії у 4,2 раза при додаванні у концентрації 50 мг/100 г. Значення константи швидкості взаємодії пероксидних радикалів з інгібітором (K_7) для одержаних антиоксидантів становило 10^6 моль/л·сек.

Висновки. Запропонований метод одержання концентратів токоферолів з відходів дезодорації соняшникової олії. Доведено ефективність одержаного концентрату токоферолів як антиоксиданту.

Ключові слова: *токоферол, деодистилят, антиоксидант, окиснення, адсорбція.*

Ароматична характеристика та загальний леткий склад червоних вин з регіону центральної північної Болгарії

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Вступ. Ароматичний потенціал вина визначається наявністю і різноманітністю сполук груп ефірів, вищих спиртів, альдегідів, монотерпенів, метоксипіразинів, аліфатиків, фенілпропаноїдів та інших.

Матеріали і методи. Об'єктом дослідження стали червоні вина, отримані з сортів винограду Рубін, Сторгозія, Букет, Трапезиця, Кайлашки, Рубін Кайлашки та Піно Нуар. Вміст алкоголю в отриманих винах було визначено за допомогою автоматичної

дистиляційною установкою Gibertini (Італія). Ароматичні компоненти у винних дистилятах визначалися за допомогою газової хроматографії.

Результати і обговорення. Виявлено 28 летких сполук. Найбільшу кількість летких сполук (22) виявлено у червоному вині сорту Рубін. Встановлено найнижчий вміст (11 ідентифікованих сполук) у вині зі Сторгозії.

Зважаючи на загальний вміст летких сполук, найменша їх кількість виявлена у вині з винограду Трапезиця (368,41 мг/дм$^{-3}$). Найвищий загальний вміст летких сполук виявлено у вині з винограду Кайлашки (1202,55 мг/дм$^{-3}$).

Загальна кількість вищих спиртів найменша (101,48 мг/дм$^{-3}$) у вині Рубін. Ця кількість була значно нижчою порівняно з результатами за цим показником у всіх досліджених червоних винах. Найбільший вміст вищих спиртів (504,84 мг/дм$^{-3}$) виявлено у червоному винні з винограду Кайлашки. У досліджених винах виявлено одиночний альдегід – ацетальдегід. Високий загальний вміст ефіру (501,79 мг/дм$^{-3}$) виявлено у червоному вині Кайлашки. У досліджених винах виявлено п'ять терпенових спиртів.

Висновки. Червоні вина, отримані зі змішаних болгарських сортів (отриманих внутрішньо- та ітеровидовою сумішшю), характеризувалися складним і різноманітним летким складом, подібним до складу Vitis vinifera L.

Ключові слова: *вино, Болгарія, ефір, вищі спирти, терпен.*

Визначення консистенції концентрованих дисперсних систем методом гравітаційної пенетрації

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Вступ. Проведені аналітичні та експериментальні дослідження консистенції дисперсних систем новим методом – гравітаційної пенетрації.

Матеріали і методи. Досліджуються дисперсні системи – паштетні продукти з м'яса птиці, механічно відокремленого. Консистенція визначалась методом гравітаційної пенетрації. Показники пенетрації визначені на основі математичного моделювання руху індентору в шарі продукту на основі диференціальних рівнянь руху другого порядку.

Результати і обговорення. Запропонований метод визначення консистенції простий у використанні. Представлені рахункові залежності і математичні моделі базуються на фізичних константах, що робить метод гравітаційної пенетрації універсальним для широкого практичного застосування при оцінці якості харчових продуктів експрес-методом.

Для проведення порівняльного аналізу консистенції харчових продуктів, отриманих за різних технологічних режимів або рецептур, запропоновано використовувати порівняльну характеристику у вигляді коефіцієнта К. Його величину розраховують як відношення глибини занурення голки у шар продукту при падінні пенетрометра з однієї висоти.

Найбільші показники мав зразок № 4, який містить 40% м'яса птиці, механічно відокремленого, та 8% рисового борошна, а найменші – зразок № 2, який містить 30% м'яса птиці, механічно відокремленого, та 10% рисового борошна.

Висновок. Визначення методу гравітаційної пенетрації розширює можливості отримання точних результатів, якщо порівняти з використанням наявних методів і апріорних формул.

***Ключові слова**: гравітаційний пенетрометр, пенетрація, консистенція.*

Вплив традиційних дріжджів кумису, вироблених у Туреччині, на деякі властивості та карбонільні сполуки кумису

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Вступ. Досліджувався кумис, вироблений з різних видів молока (кобилячого, коров'ячого та козячого), та визначалася зміна ароматичних сполук і утворень біогенних амінів протягом 30 днів.

Матеріали і методи. Кумис виробляли з використанням традиційних дріжджів. Біогенний амін, проаналізований за допомогою високоефективної рідинної хроматографії та ароматичних сполук, визначали за допомогою хроматографії в головному просторі.

Результати і обговорення. Вміст молочної кислоти (%) поступово зростав у період зберігання зразків кумису. Найбільша кількість етилового спирту спостерігалась в кумисі (30-й день), виробленому з коров'ячого молока (1,95 %). Серед біогенних амінів було виявлено, що значення путресцину є найбільш високим у кумисі, виробленому з козячого молока (5,68–5,86 проміле), тоді як значення кадаверину досягало найвищих значень (2,66–9,74 проміле) у кумисі, виробленому з кобилячого молоко. Кількість тираміну значно зросла у всіх пробах кумису. Феніл етиламін виявлено лише в кумисі з козячого молока (0,64-0,84 проміле). Вміст гістаміну був найвищим у кумисі з кобилячого молока (4,80–6,52 проміле).

Значення аромату в перший день зберігання в пробах кумису складало 0,78–3,76 проміле ацетальдегіду, 0,23–0,27 проміле ацетоїну, 0,80–1,62 проміле діацетилу, 0,03–0,06 проміле метанолу, 7,27–14,73 проміле ацетату. Не було виявлено статистично значущої різниці між ароматичними сполуками за рівнем молока.

Висновки. Біогенні аміни в кумисі, вироблені традиційними дріжджами кумису з різних видів молока в Туреччині, були нижчими за максимально допустиму дозу токсичності. Щодо ароматичних сполук, то молочні типи статистично однаково впливають на ароматичні сполуки.

Ключові слова: *кумис, дріжджі, біогенний амін, аромат, карбоніл.*

Ефективність використання композиції мінералізованих солодів для збагачення харчових продуктів мікронутрієнтами

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Вступ. Мета досліджень – отримання та дослідження складу солодів з підвищеним вмістом дефіцитних нутрієнтів і збагачення обраною сировиною житньо-пшеничного хліба.

Матеріали і методи. Для отримання мінералізованої зернової сировини зерно кукурудзи та вівса пророщували із застосуванням розчинів солей цинку ($ZnSO_4$) та хрому ($CrK(SO_4)_2 \times 10H_2O$) різних концентрацій: 0,001%, 0,002%, 0,003%, 0,004%, 0,005%. Для визначення мінерального складу зерна та солоду застосовували рентгенофлуоресцентний аналіз і метод інверсійної вольтамперометрії для визначення вмісту цинку.

Результати і обговорення. Оптимальна концентрація солі цинку і замочувальній воді склала 0,002 %, при цьому вміст цинку у збагаченому зерні кукурудзи зріс у 6,7 раза порівняно з вихідним зерном. Для збагачення зерна іонами хрому концентрація солі хрому в замочувальній воді не повинна перевищувати 0,001 %. За даними рентгенофлуоресцентного аналізу вміст мінеральних речовин у збагаченому солоді зростає, вміст цинку, якщо порівняти з вихідним солодом, збільшується в 6 разів, а хрому – втричі, що вказує на можливість корегування мінерального складу вихідної сировини шляхом замочування і пророщування зерна у водних розчинах солей мікроелементів.

Для збагачення харчових продуктів мінералізованими солодами як традиційний продукт у цьому дослідженні обрано житньо-пшеничний хліб. Мінералізовані солоди позитивно впливають на підйомну силу дріжджів, і в більшій мірі – при додаванні солей цинку. Це свідчить про скорочення тривалості технологічного процесу.

Дослідження впливу масової частки внесених мінералізованих солодів на якісні показники житньо-пшеничного хліба показали, що оптимальною є кількість 10 % до маси борошна.

Висновки. Додавання композиції мінералізованих солодів до рецептури харчових продуктів збагачує їх біологічно активними речовинами та надає функціональних властивостей.

Ключові слова: *кукурудза, овес, солод, цинк, хром.*

Перспективність використання козячого молока у виробництві сирів сичужних м'яких

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Вступ. Метою дослідження є аналіз хімічного складу, харчової цінності та технологічних властивостей козячого молока як потенційно перспективної сировини для виробництва м’яких сирів.

Матеріали і методи. Об'єкт досліджень – молоко козяче незбиране як сировина у виробництві сирів сичужних м'яких.

Результати і обговорення. Біохімічні й технологічні властивості унікальних якостей козячого молока маловідомі, через що цей продукт майже не використовується. Нова концепція виробництва продуктів, яка краще відповідатиме потребам людини, до цього часу не застосовувалася до козячого молока та продуктів його переробки.

Одним із перспективних напрямів є виробництво м'яких сирів. На сьогодні розроблено технології м'яких сирів з використанням підвищеної кількості бактеріальних препаратів та сичужного ферменту, додаванням розчинів органічних кислот, ультразвуковим обробленням молока чи його концентруванням методом ультрафільтрації. За кількістю розробок, у яких реалізуються принципи харчової комбінаторики, пріоритет належить виробництву комбінованих продуктів, в яких сировина тваринного походження поєднується з рослинними компонентами.

У технології м'яких сирів застосовують овочеві культури у вигляді сухих порошків, продукти переробки бобових, екструдоване борошно із зародків насіння нуту, борошно амаранту.

Потенціал розвитку виробництва м'яких сирів на основі козячого молока відповідає двом трендам – користь продукту завдяки використанню біологічно цінної сировини та ресурсозбереження і збільшення промислових об'ємів переробки козячого молока та розробка нових технологій.

Висновки. Застосування прянощів дасть змогу покращити та урізноманітнити смако-ароматичні властивості сирів на основі козячого молока, збагатити їх комплексом біологічно активних речовин, збільшити вихід продуктів і підвищити їх стабільність під час зберігання.

Ключові слова: *молоко, коза, сир, прянощі, гуньба сінна, куркума.*

Ботанічний і фізико-хімічний аналіз меду з оманської та білої акації

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Вступ. Споживач на ринку Близького Сходу має складності із розрізненням двох видів акацієвого меду: «Справжнього акацієвого» з *акації Tortilis* та з *псевдоакації Robinia.*

Матеріали і методи. Ботанічні та фізико-хімічні характеристики визначалися для зразків меду з *акації Tortilis* та *псевдоакації Robinia.* Ацетолізований пилок з меду використовували для визначення концентрації, чистоти та квіткового походження.

Результати і обговорення. Мед з *акації Tortilis* мав середній рівень pH 4,83, вміст вологи 16,75 %, електичну провідність 1,82 mS/см, вільну кислотність 95,30 мекв/кг, активність діастази (діастазне число) 12 та інвертазну активність 141,07 Од/кг, які є відносно вищими за нормативні характеристиками, за винятком електричної провідності та вільної кислотності. Зразки меду з *псевдоакації Robinia* мають pH 3,80, вміст вологи 17,41%, електичну провідність 0,33 mS/см, вільну кислотність 8,03 мекв/кг, активність діастази (діастазне число) 8,00 та інвертазну активність 17,53 Од/кг. Ці значення відповідають стандартам. Екстракт меду з *акації Tortilis* співвідносився з pH,

вмістом вологи, вільною кислотністю, діастазою та інвертазою, що свідчить про значний вміст мінералів і органічних кислот. Усі параметри меду з *акації Tortilis* були вищими, ніж меду з *псевдоакації Robinia.*

Висновок. Рекомендується маркування меду конкретними назвами. Ми пропонуємо назву «Акація» для меду з *акації Tortilis* та «Робінія» – для меду з *псевдоакації Robinia.*

Ключові слова: *мед, акація, псевдоакація Robinia.*

Удосконалення технології виробництва безалкогольних напоїв з використанням нетрадиційної сировини

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Вступ. Досліджено технологію виробництва безалкогольних напоїв з використанням нетрадиційної сировини з метою удосконалення та розширення асортименту продукції.

Матеріали і методи. Для удосконалення технології безалкогольного напою використано екстракт полуниці та малини. Кількість поліфенолів в об'єктах дослідження визначено спектрофотометричним методом. Оптичну щільність вимірювали в кюветі з товщиною шару 10 мм на спектрофотометрі SF-46.

Результати і обговорення. Вміст фенольних сполук має вирішальне значення для стабільності напоїв. Використання морфологічних частинок сировини дає змогу не тільки поліпшити органолептичні властивості напоїв, а й збільшити їх стабільність. Екстракт порошку малини (2,30 і 1,02) має кращі показники вмісту фенольних сполук і рутину, ніж екстракт порошку полуниці (1,50 і 0,30).

Наявні дані свідчать про те, що частини рослин містять не менше біологічно активних речовин, а іноді навіть більше, ніж фрукти, ягоди та овочі, а їх використання дає змогу отримувати з них концентрати та напої з м'яким, пікантним, гармонійно індивідуальним смаком і ароматом.

Орієнтуючись на багатий вміст цінних компонентів, листя та стебла малини і полуниці досліджували на предмет використання добавок до концентрату безалкогольних напоїв.

Екстракт, який готують шляхом кип'ятіння подрібненого листя і гілочок у воді протягом 3 хв, володіє кращими органолептичними властивостями порівняно з іншими зразками, тому цей спосіб приготування екстракту малини є оптимальним. Полуниця з експерименту була виключена через насичені трав'янисті тони в смаку і відповідний аромат. 0,75 г і 1,0 г в 100 $см^3$ екстракту малини найкраще підходять для використання з метою створення основи для безалкогольного напою.

Висновки. Використання екстрактів нетрадиційної рослинної сировини допоможе покращити органолептичні властивості безалкогольного напою та розширити асортимент.

Ключові слова: *полуниця, малина, солод, екстракт, стабільність.*

Деякі аспекти використання нанотехнологій у харчовій промисловості

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Вступ. Наведено дані літературного огляду сучасних напрямків застосування нанотехнологій у промисловості, описано їхні властивості та особливості взаємодії з біополімерами в складі харчових продуктів.

Результати і обговорення. TiO_2, ZnO і SiO_2 є найбільш поширеними наночастинками, які використовуються при отриманні продуктів харчування або інгредієнтів, пов'язаних з харчовими продуктами.

Харчова добавка Е551 (діоксид кремнію SiO_2) в основному використовується як антизлежувач для покращення сипучості порошкоподібних або гранульованих продукті і таким чином запобігає утворенню грудок. Нині нанорозмірний SiO_2 є однією з найпоширеніших нанодобавок у різних галузях харчової промисловості. Наукові дослідження показують, що кремнезем, завдяки особливостям будови та великій площі поверхні, володіє високими адсорбційними властивостями, якщо порівняти з водою, білками, екзо- і ендотоксинами, патогенними мікроорганізмами.

Численні дослідження підтверджують можливість ефективної модифікації реологічних характеристик камедей під час їх спільного використання з кремнеземом у складі функціонально-технологічних композицій.

Експериментальним методом встановлено, що внесення SiO_2 у гідратовані соєві білки та колагеновмісні білкові препарати призводило до ущільнення консистенції, модифікуючи реологічні і функціональні властивості.

Проведені наукові дослідження використання нанокомпозиту в технології м'ясомістких кулінарних напівфабрикатів підтверджують ефективність використання високодисперсного кремнезему як текстуроформуючої добавки.

Згідно з європейським законодавством, при наявності в складі харчового продукту нанокомпозитів нанесення на етикетку терміна «нано» здійснюється лише тоді, коли близько 50% частинок мають розмір у діапазоні 1–100 нм.

Висновки. Наночастинки безпосередньо впливають на поглинання і засвоєння поживних речовин за рахунок фізико-хімічних модифікацій, які відбуваються при взаємодії харчових компонентів з наночастинками.

Ключові слова: *нанотехнології, діоксид кремнію, харчовий продукт, камедь, м'ясо, синергізм.*

Раціональні параметри миття тонкорунної вовни

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Вступ. Комбінування поверхнево-активних речовин (ПАР) Sles 70 з апротонним органічним розчинником диметилсульфоксидом (ДМСО) дає змогу створити нейтральний мийний засіб, що потребує дотримання раціональних режимів миття вовни. Тож мета дослідження полягала у виявленні раціональних параметрів миття тонкорунної вовни.

Матеріали і методи. За латинськими квадратами сплановано та проведено експеримент з визначенням впливу концентрації Sles 70 у мийному розчині в діапазоні 0,1–3,1 г/дм^3, концентрації ДМСО 0,01–0,61 г/дм^3, гідромодуля 10–100, температури 30–48 °С на очищення тонкорунної вовни під час миття вовняного волокна вказаним комбінованим мийним засобом.

Результати і обговорення. У досліджуваному діапазоні варіювання факторів найістотніше проявився вплив гідромодуля на очищення вовни і на вилучення екстрактивних речовин з поверхні волокна у відпрацьований мийний розчин.

Гідромодуль 40 і більший дає змогу очистити вовну від жиру і забруднень. Температура має стабільний вплив у заданому діапазоні, тому всі досліджені значення температури сприяють вилученню жирових забруднень вовни за такого компонентного складу мийного розчину.

За гідромодуля 70 і 100, а також концентрації 1 % мас. Sles 70, тобто за концентрацій ПАР, що перевищують критичну концентрацію міцелоутворення (ККМ), волокна вовни також очищаються під час миття. Логічно відзначити, що за концентрацій ПАР, нижчих за ККМ, ефективність очищення вовни знижується. Концентрація ДМСО також мала незначний вплив на очищення вовни порівняно з гідромодулем.

Висновки. Раціональним режимом однократного миття вовни є використання гідромодуля 40, концентрації 1 % мас. Sles 70 і концентрації ДМСО до 0,61 г/дм^3 у діапазоні температур 30–48 °С. Якість миття можна поліпшити, збільшуючи гідромодуль одноразового миття або проводячи кількаразове миття за мінімального гідромодуля.

Ключові слова: *вовна, жир, миття, ПАР.*

Процеси, обладнання і системи контролю

Методи оброблення рідких систем і розчинів: огляд

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Вступ. Проведено аналітичні дослідження застосування різних методів оброблення водних систем і розчинів з метою зміни хімічних і фізичних параметрів та властивостей цих систем і розчинів.

Матеріали і методи. Об’єктом наукового дослідження є різні методи та способи оброблення рідких водних систем і розчинів для технологічних потреб у харчових виробництвах. Предметом дослідження є зміна фізичних і хімічних параметрів та властивостей водних систем і розчинів. Для досліджень використовувались аналітичні методи, зокрема критичний огляд наукових і науково-дослідних робіт, оглядів, статей, монографій щодо різних методів та способів оброблення водних систем і розчинів.

Результати і обговорення. Встановлено, що значна кількість методів оброблення водних систем, які широко застосовуються у різних галузях харчової промисловості, є недостатньо вивченою. Застосування кожного з методів оброблення залежить від багатьох факторів.

Аналітичні дослідження показали можливість застосування новітніх методів оброблення безреагентного типу або фізичного впливу. Кожен з цих методів, способів і технологічних режимів має власні об'єктивні невирішені проблеми, які потребують нестандартних підходів.

Хімічні методи оброблення дають змогу проводити дезінфекційну обробку, інактиваційну щодо патогенних організмів. Особливою перевагою цих методів є можливість використання за великих потужностей виробництв.

Біологічні методи оброблення водних систем і розчинів є важливими та займають вагоме місце у процесах рециркуляційної переробки й очищення забруднених і відпрацьованих вод.

Такі фізичні та хімічні властивості і параметри води, водних систем і розчинів, як окисно-відновний потенціал, водневий показник, кількість розчиненого кисню тощо, можуть змінюватись завдяки застосуванню методів фізичного впливу.

Висновки. Застосування різних поєднань і комбінацій методів водооброблення може покращити екологічну безпеку. Застосування методу дискретно-імпульсного введення енергії дає змогу значно підвищити продуктивність, скоротити тривалість процесу оброблення, зменшити витрати сировинних ресурсів, знизити енерговитрати.

Ключові слова: *вода, рідкий, гідратований, оброблення, тиск.*

Аналіз причин, обставин і наслідків виробничого травматизму на підприємствах харчової промисловості при виробництві напоїв

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Вступ. Мета дослідження – визначити причини, наслідки та обставини виробничого травматизму на підприємствах харчової промисловості при виробництві напоїв за період з 2010 р. по 2018 р. в Україні.

Матеріали і методи. Під час проведення дослідження застосовано прикладний статистичний аналіз даних про нещасні випадки, що трапилися на підприємствах харчової промисловості при виробництві напоїв за період з 2010 р. по 2018 р.; метод головних компонент. Дослідження трендів часових рядів виробничого травматизму базується на даних Державної служби статистики України.

Результати і обговорення. На підприємствах харчової промисловості при виробництві напоїв було травмовано 221 працівника на харчових підприємствах при виробництві напоїв, з них загинуло 35 осіб. З них 75,6% травм отримано особами чоловічої статі, на жіночу стать припадає 24,4 %, що у 3 рази менше від рівня травматизму чоловіків. Організаційні фактори призводять до 80% виробничих травм, найпоширенішими організаційними причинами стали: порушення правил безпеки руху (12,8 %), порушення трудової і виробничої дисципліни (11,2%), недоліки під час навчання безпечним прийомам праці (9 %), невиконання вимог інструкцій з охорони праці (8,2 %) від загальної кількості травмованих працівників харчової промисловості при виробництві напоїв; порушення вимог безпеки під час експлуатації обладнання, устаткування, машин, механізмів (7,4%), невиконання посадових обов'язків, відсутність належного контролю з боку посадових осіб (5,4%).

Серед технічних причин домінують: конструктивні недоліки, недосконаліть, недостатня надійність засобів виробництва, транспортних засобів (5,4%);

незадовільний технічний стан виробничих об'єктів, будівель, споруд, інженерних комунікацій, території (3,6%); недосконаліть технологічного процесу, його невідповідності вимогам безпеки (2%).

Висновки. Організаційні фактори призводять до 80% виробничих травм, з них більше ніж 63% усіх припадає на працівників віком від 30 до 50 років. В основному порушення відбуваються через необізнаність робітників з правилами безпеки.

Ключові слова: *безпека, праця, підприємство, травматизм.*

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Requirements for article:
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Всі елементи після року видання розділяються **комами**.

Приклади:

1. Yannick Fayolle, Sylvie Gillot, Arnaud Cockx, Laetitia Bensimhon, Michel Roustan, Alain Heduit (2010), In situ characterization of local hydrodynamic parameters in closed-loop aeration tanks, *Chemical Engineering Journal*, 158(2), pp. 207–212.
2. Carlo Tocchi, Ermanno Federici, Laura Fidati, Rodolfo Manzi, Vittorio Vincigurerra, Maurizio Petruccioli (2012), Aerobic treatment of dairy wastewater in an industrial three-reactor plant: Effect of aeration regime on performances and on protozoan and bacterial communities, *Water Research*, 46(10), pp. 3334–3344.

Приклад оформлення статті, оригінал якої українською мовою:

1. Pyroh T.P., Konon A.D., Skochko A.B. (2011), Vykorystannia mikrobnykh poverkhnevo-aktyvnykh rechovyn u biolohii ta medytsyni, *Biotekhnolohiia*, 4(2), pp. 24–38.

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Посилання на книгу

Автори (рік), *Назва книги (курсивом)*, Видавництво, Місто.

Всі елементи після року видання розділяються комами.

Приклади:

1. Harris L. (1991), *Money theory*, McGraw-Hill Companies, Hardcover
2. Rob Steele (2004), *Understanding and measuring the shelf-life of food*, CRC Press.

Приклад оформлення статті, оригінал якої українською або російською мовою:

1. Kirianova H.A. (2008), Udoskonalennia tekhnolohii termostabilnykh zheleinykh nachynok shliakhom ratsionalnoho vykorystannia hidrokoloidiv roslynnoho ta mikrobnoho pokhodzhennia: PhD tethis, NUHT, Kyiv.
2. Zalutskyi I.R., Tsymbaliuk V.M., Shevchenko C. H. (2009), Planuvannia i diahnostyka diialnosti pidpryiemstva, Novyi svit, Lviv.

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Приклад посилання на статтю із електронного видання:

1. Barbara Chmielewska. (2012), Differentiation of the standard of living of families in countries of the European Union, *Ukrainian Food Journal*, 2(2), pp. 230–241, available at: http://ufj.ho.ua/Archiv/UKRAINIAN%20FOOD%20JOURNAL%202013%20V.2%20Is.2.pdf
2. (2013), *Svitovi naukovometrychni bazy*, available at: http://www1.nas.gov.ua/publications/q_a/Pages/scopus.aspx

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