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## Study of the structure of food emulsifiers of acylglycerine origin by infrared spectroscopy

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### Abstract

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**Introduction.** The structure of food emulsifiers obtained on the basis of the refined sunflower oil under mild conditions is studied for the purpose of determination of the content of mono- and diacylglycerines of fatty acids and proof of the conservation of essential bioactive components in them and deceleration of thermal-oxidative processes.

**Materials and methods.** A qualitative and quantitative study of emulsifiers of acylglycerine origin obtained under mild conditions (35...40 °C) is performed by using infrared spectroscopy on Perkin-Elmer Spectrum One FTIR Spectrometer by the method of a crushed drop.

**Results and discussion.** Infrared spectra of the new emulsifiers of acylglycerine origin are studied and an analysis of the characteristic absorption bands assigned to the respective types of valence and deformation vibrations of triacylglycerines (1110, 1173, 1244 cm<sup>-1</sup> —  $\nu(\text{C}=\text{O})$  of esters; 1377 and 1416 cm<sup>-1</sup> —  $\delta_s(\text{C}-\text{H})$  in groups —CH<sub>3</sub> and —CH<sub>2</sub>—; 1736 cm<sup>-1</sup> —  $\nu(\text{C}=\text{O})$  of esters; 2855 and 2927 cm<sup>-1</sup> —  $\nu(\text{C}-\text{H})$  in —CH<sub>2</sub>— groups; 3009 cm<sup>-1</sup> —  $\nu_{as}(\text{C}-\text{H})$  in groups —CH=CH— in the *cis*-form), the hydroxyl groups of mono-, diacylglycerines of fatty acids (3435 cm<sup>-1</sup>), primary alcohols (1061 cm<sup>-1</sup>) is made. The presence of mono- and diacylglycerines of fatty acids in the new emulsifiers is proved. Due to the mild conditions of their obtaining these emulsifiers don't contain *trans*-isomers and unsaturated acids in the native form are preserved in them. On the basis of calculated spectral characteristics (peak intensity, width of the absorption band, area *S* bounded by the curve and the horizontal zero line) the calibration graph of *S* on the mass concentration of mono-, diacylglycerines in the model compositions E471 with the refined sunflower oil is plotted. With the help of the obtained line equation the total content of mono-, diacylglycerines of fatty carboxylic acids in the new food emulsifiers is determined as 54,2±1,2%.

**Conclusions.** Using the method of infrared spectroscopy for solving the problems of quantitative determination of mono-, diacylglycerines of fatty acids in the emulsifiers of series of acylglycerines E471 is suggested.

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## Introduction

Currently there is an increasing demand for high quality foodstuff that is made with the using additives based on natural raw materials that are absolutely harmless to the human health and the environment. Such additives include mono- and diacylglycerines (MAG and DAG) of fatty acids (E471) — safe additives of the GRAS status (Generally Regarded as Safe — completely safe) that are applied without restrictions. Being surfactants with an indicator of hydrophilic-lipophilic balance (HLB) 3...4 they are widely used as lipophilic nonionic emulsifiers, emulsion stabilizers, baking powders, and amendments. In publications [1-3] significant advantages of emulsifiers of acylglycerine series are noticed. For example, they can improve the consistence, marketable state of the finished meat products; increase their yield due to the thermal treatment [4-7].

In spite of the quite wide assortment of these emulsifiers there are significant drawbacks in the technology of their obtaining. First of all, these drawbacks are associated with the hard conditions of the synthesis of emulsifiers [8]. Moreover, their industrial production in Ukraine is absent.

The technology of producing emulsifiers of E471 series is based on two chemical processes that are carried out in industry at 210...245 °C: glycerolysis of fats (transesterification with glycerine) and esterification of glycerine with high molecular fatty acids. A mixture of the products obtained is separated by centrifugation and molecular distillation at temperatures 205...210 °C. Along with the high yields of MAG (40...50%) industrial technologies are notable for hard conditions of glycerolysis and molecular distillation thus causing the intensification of thermal oxidation and thermal polymerization processes in the emulsifiers [8]. New technologies of production of emulsifiers also have the similar drawbacks as they assume the technological processes to be carried out at temperatures not below 120 °C [9-10]. The enzymatic synthesis technologies which are being actively developed now have such a distinctive feature as a duration of the process (2 to 8·60<sup>2</sup> seconds) [11].

The domestic market of food emulsifiers is mainly represented with additives E471 and their derivatives (E472a-g) of foreign production for using primarily in confectionery and perfume industry [12]. Usually emulsifiers E471 don't contain polyunsaturated fatty acids as they are produced in industry by means of glycerolysis of palm oil with formation of MAG of saturated fatty acids [13].

Thus development of the technology of producing domestic food emulsifiers from the natural raw materials under the mild conditions was an important task. In the previous works authors based the technology of obtaining food emulsifiers with mono-, diacylglycerines of fatty acids under mild conditions (at 35...40 °C). New food emulsifiers of acylglycerine origin for meat products were obtained as an oil phase with MAG, DAG by means of transesterification of the refined sunflower oil in the hexane-isopropanol system [14].

Therefore qualitative and quantitative studies of the composition of these emulsifiers for the purpose of determination of the content of surface active components — mono- and diacylglycerines of fatty acids and proof of the conservation of essential bioactive components and deceleration of thermal-oxidative processes in these emulsifiers gain actuality.

## Materials and methods

The current studies deal with emulsifiers of acylglycerine origin obtained on the laboratory equipment under the mild conditions according to the authors' developed technology of transesterification of the refined sunflower oil in a binary system of organic solvents as follows. Prepared 1.5...1.6% solution of potassium hydroxide in isopropanol, based on the mass ratio of refined sunflower oil:hexane:isopropanol — 1:2,5:2,5, was introduced into the miscella with a mass fraction of 28...30% (refined sunflower oil in hexane) and transesterification was performed under constant stirring within (10...12)·60 seconds at temperature 35...40 °C. In order to complete transesterification water was introduced into the binary system in amount 16...18% from the system mass while stirring. The diphasic system was kept at 23...25 °C until complete separation of the water-isopropanol layer with soaps, partly MAG, DAG *etc.* from the hexane layer containing TAG, DAG, MAG. Evaporation of hexane from miscella was performed in the rotary evaporator IP-1M2 within (5...10)·60 seconds at 40 °C under the pressure of 335 mbar. Emulsifiers of acylglycerine origin were obtained as an oil phase (with MAG, DAG) of a light yellow color (this is typical for glycerines of unsaturated fatty acids) with a neutral taste, without smell.

For the quantitative determination of MAG, DAG and plotting the calibration graph the model compositions of emulsifiers with the total mass fraction of MAG, DAG of 10, 20, 30, 40% were prepared by mechanical mixing of the refined sunflower oil (Ukraine) and the emulsifier E471 (Malaysia) with a known composition (content of mono- and diacylglycerines — 95,5±2,5% and 3,5±0,1% respectively).

A qualitative and quantitative study of emulsifiers of acylglycerine origin and model compositions was performed by using infrared spectroscopy on Perkin-Elmer Spectrum One FTIR Spectrometer by the method of a crushed drop. The drops of samples were placed in a thin layer between the plates from Zinc Selenide while recording IR spectra.

## Results and discussion

IR spectra of the new emulsifiers of acylglycerine origin (Fig. 1) are represented with characteristic absorption bands assigned to the respective types of valence  $\nu$  and deformation  $\delta$  vibrations of triacylglycerines: a triad of bands 1110  $\text{cm}^{-1}$ , 1173  $\text{cm}^{-1}$ , 1244  $\text{cm}^{-1}$   $\nu(\text{C}=\text{O})$  of esters; 1377  $\text{cm}^{-1}$  and 1416  $\text{cm}^{-1}$  —  $\delta_s(\text{C}-\text{H})$  in groups  $-\text{CH}_3$  and  $-\text{CH}_2-$ ; 1736  $\text{cm}^{-1}$  —  $\nu(\text{C}=\text{O})$  of esters; 2855  $\text{cm}^{-1}$  and 2927  $\text{cm}^{-1}$  —  $\nu(\text{C}-\text{H})$  in groups  $-\text{CH}_2-$ ; 3009  $\text{cm}^{-1}$  —  $\nu_{as}(\text{C}-\text{H})$  in groups  $-\text{CH}=\text{CH}-$  in *cis*-form.

The absence of absorption bands at 970  $\text{cm}^{-1}$ , 1675...1665  $\text{cm}^{-1}$  indicates that obtained under mild conditions emulsifiers don't contain *trans*-isomers. The presence of absorption bands at 1657  $\text{cm}^{-1}$  and 3009  $\text{cm}^{-1}$  proves the conservation of unsaturated acids in the native state on the level of their content in the sunflower oil [15].

The presence of mono- and diacylglycerines of fatty acids in the emulsifiers is confirmed by the broad band registered at 3435  $\text{cm}^{-1}$  (Fig. 1) that is characteristic for the valence vibrations of hydroxyl groups associated by hydrogen bonds (3350±100  $\text{cm}^{-1}$ ), by band at 1061  $\text{cm}^{-1}$  that is characteristic for the valence vibrations of hydroxyl groups of the primary alcohols.



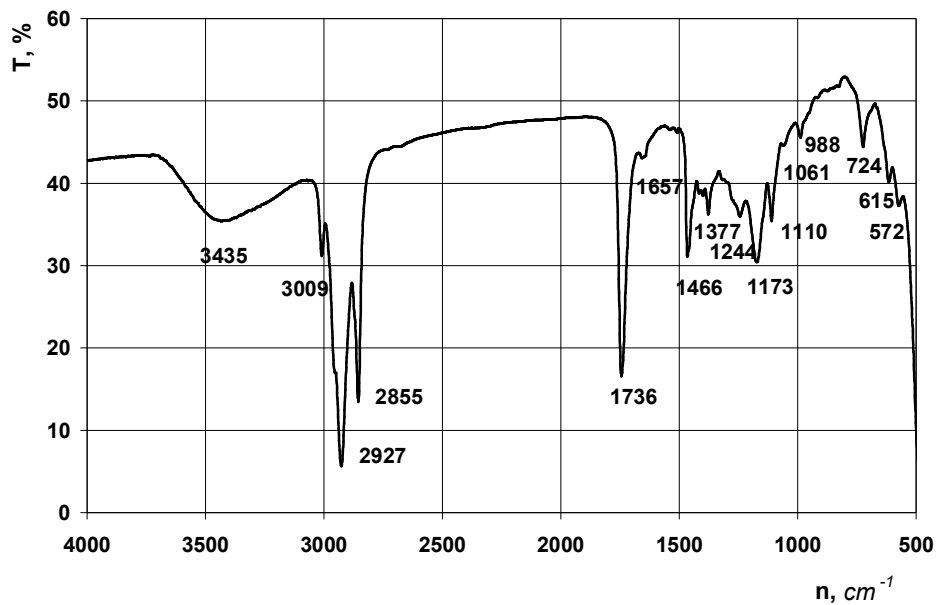


Fig. 1. IR absorption spectrum of the sample of emulsifiers of acylglycerine origin

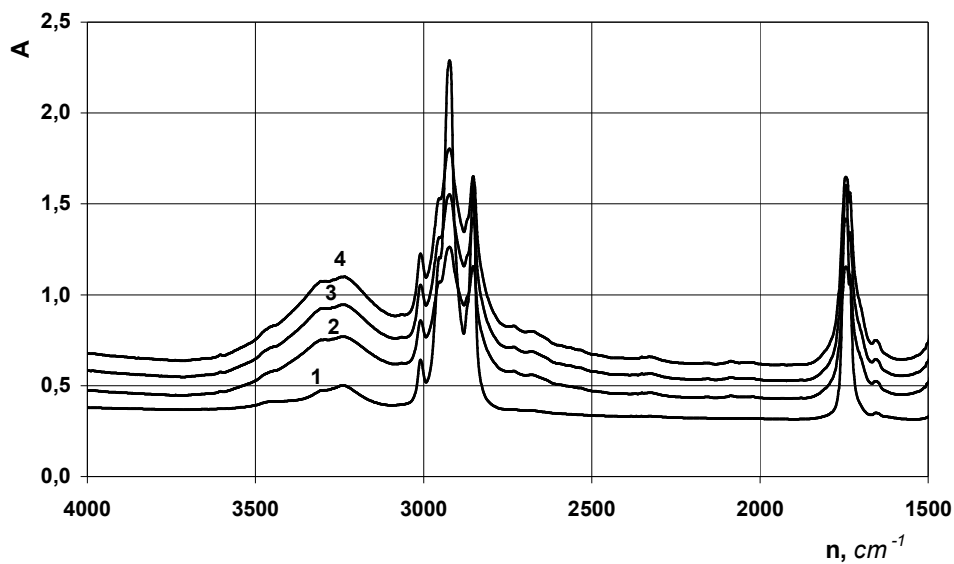


Fig. 2. IR spectra of the samples of model compositions of emulsifiers with different mass fraction of MAG, DAG, %:  
1 – 10; 2 – 20; 3 – 30; 4 – 40

IR spectroscopy allows solving problems of quantitative analysis. Therefore it was applied for determining the mass fraction of MAG and DAG in the test emulsifiers of E471 series in the spectral area that was characteristic for the valence vibrations of associated hydroxyl groups —  $3350 \pm 100 \text{ cm}^{-1}$ . IR spectra of the samples of model compositions of emulsifiers on the basis of the refined sunflower oil and E471 with the total mass fraction of MAG, DAG — 10, 20, 30, 40% were obtained (Fig. 2).

It is known [16] that IR spectroscopy uses integral intensity (absorption coefficient) that is considered as the sum of all the values of the extinction coefficient  $\varepsilon$  within the whole absorption band regarded, *i.e.* the area bounded by the curve and the x axis. The integral intensity is equal to the area of the band and, in case if the absorption coefficient and wave number  $\nu$  ( $\text{cm}^{-1}$ ) are chosen as coordinates; it is expressed [16] by the integral:

$$A_\nu = 2,304 \int_{\nu_1}^{\nu_2} \varepsilon d\nu \quad (1)$$

The integral intensity is less dependent on the apparatus resolution than the intensity at the maximum and is better reproduced. The dependence of the optical density on the wave number  $\nu$  by the outline of the band assuming the band is symmetrical with respect to the maximum and does not overlap with the other bands is described by Lorentzian function [16]:

$$A_\nu = a / [(\nu - \nu_{\max})^2 + b^2], \quad (2)$$

where  $a$ ,  $b$  — are constants.

The function 2 describes the band better the broader is the band. Since this approximation is satisfactory for the broad band of associated hydroxyl groups at  $3350 \pm 100 \text{ cm}^{-1}$ , the area  $S$  bounded by the curve and the horizontal zero line ( $A = 0$ ) can be described by the equation [16]:

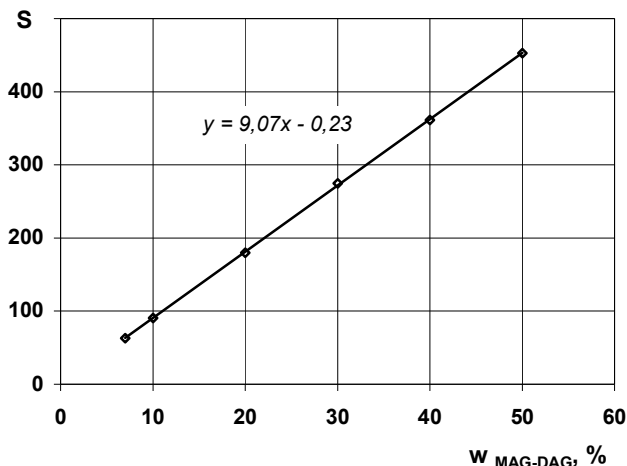
$$S = (\pi/2) \cdot \Delta\nu_{1/2} \cdot A_{\max}, \quad (3)$$

where  $\Delta\nu_{1/2}$  — the width of the absorption band between the points of the curve where the optical density is equal to the half of the maximum one;

$A_{\max}$  — peak intensity.

Based on the calculated spectral characteristics (peak intensity, the width of the absorption band, the area  $S$  bounded by the curve and the horizontal zero line) the calibration curve representing the dependence of  $S$  value on the mass fraction of MAG-DAG ( $w_{\text{MAG-DAG}}$ ) in the model compositions of emulsifiers E471 with the refined sunflower oil was plotted (Fig. 3).

The obtained dependence is well described by a linear function that allows using it as a calibration curve for determining the mass fraction of MAG and DAG contained in the emulsifiers of E471 series which the emulsifiers of acylglycerine origin obtained under mild conditions also belong to. Using the obtained equation of the line  $S = 9,07 \cdot w_{\text{MAG-DAG}} - 0,23$  the amount of  $w_{\text{MAG-DAG}}$  in the new emulsifiers studied was calculated.



**Fig. 3. Calibration curve of the dependence of MAG, DAG content in the model compositions of emulsifiers E471**

The content of MAG, DAG in the new emulsifiers obtained at temperature 35...40 °C in the system hexane-isopropanol from the refined sunflower oil was 54,2±1,2%. The data obtained correlates with the results of determination by thin-layer chromatography with a relative deviation of the mass fraction of MAG and DAG within 1,1...2,4%. The results of the studies confirm the possibility of using IR spectroscopy for solving the problems of quantitative determination of mono-, diacylglycerines of fatty acids in the emulsifiers of acylglycerine E471 series.

## Conclusions

Using infrared spectra the presence of the characteristic absorption bands assigned to the respective types of valence and deformation vibrations of triacylglycerines in the new emulsifiers of acylglycerine origin was proved:  $\nu(\text{C}=\text{O})$  — 1110  $\text{cm}^{-1}$ , 1173  $\text{cm}^{-1}$ , 1244  $\text{cm}^{-1}$ ;  $\delta_s(\text{C}-\text{H})$  — 1377  $\text{cm}^{-1}$  и 1416  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{O})$  — 1736  $\text{cm}^{-1}$ ;  $\nu(\text{C}-\text{H})$ : 2855  $\text{cm}^{-1}$  и 2927  $\text{cm}^{-1}$ ;  $\nu_{as}(\text{C}-\text{H})$  in groups  $-\text{CH}=\text{CH}-$  in the *cis*-form — 3009  $\text{cm}^{-1}$ ), hydroxyl groups of mono-, diacylglycerines of fatty acids associated by hydrogen bonds — 3435  $\text{cm}^{-1}$ , primary alcohols — 1061  $\text{cm}^{-1}$ .

The fact of the absence of absorption bands at 970  $\text{cm}^{-1}$ , 1675...1665  $\text{cm}^{-1}$  proves that obtained under mild conditions emulsifiers don't contain *trans*-isomers. The presence of absorption bands at 1657  $\text{cm}^{-1}$  and 3009  $\text{cm}^{-1}$  indicates on the conservation of unsaturated acids in the native state on the level of their content in the sunflower oil.

On the basis of calculated spectral characteristics (peak intensity, width of the absorption band, area  $S$  bounded by the curve and the horizontal zero line) the calibration graph of  $S$  on the mass concentration of mono-, diacylglycerines in the model compositions is plotted and the equation of the line  $S = 9,07 \cdot w_{\text{MAG-DAG}} - 0,23$  is determined.

By means of IR spectroscopy the total content of mono-, diacylglycerines of fatty acids in the food emulsifiers obtained under mild conditions (35...40 °C) from the refined sunflower oil is determined. This data correlates with the results obtained by means of thin-layer

chromatography. The relative deviation of the mass fraction of MAG and DAG between two methods is not more than 2,4%.

Using the method of infrared spectroscopy for solving the problems of quantitative determination of mono-, diacylglycerines of fatty acids in the emulsifiers of series E471 is suggested.

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## The changes of carotene in the process of obtaining food additives on the basis of carrots

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### Abstract

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**Introduction.** The aim of the study was to develop new technological solutions to better utilization of the properties of carrot to obtain two multifunctional dietary supplements containing carotene in dry and liquid form.

**Materials and methods.** Carrot varieties Shantanu 2461, carrot juice, husks, powdery enrichment from carrot husks containing carotene and concentrated liquid filler containing carotene were used. The chemical composition of all samples was determined according to the international standards

**Results.** The work proposed a comprehensive resource-saving technology of processing of carrots with getting two basic products that contain carotene - dry and liquid. Dry enrichment "Carrotynka" obtained under production conditions by means of microwave drying of carrot husks, has a high content of  $\beta$ -carotene (148,0-154,0 mg/100 g) and fiber (11 g/100 g). Liquid filler "Carrot honey", obtained on the basis of carrot juice (70% of dry substance) - rich sugar (52-55 g/100 g), b-carotene (up to 11-12 mg/100 g) and pectin (up to 4 g/100 g).

Obtained products were subjected to various technological influences. As a result of these tests it can be noted a relatively high stability of obtained food additives to various modes of process and be recommend them for wide use in food technology as a multifunctional enriching additives.

We had tested a number of technologies of getting canned products from restored "Carrot honey", as well as development of confectionery and bakery products of new recipes, which gave a positive result.

**Conclusion.** The obtained products containing carotene, can be used in food technology as a multifunctional enriching additives.

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## Introduction

The growing worldwide trend towards healthy food led to the development of functional product. Functional foods, due to bioactive components presence in its composition are capable to support human health and increase the body's resistance to adverse environmental factors. To correct the nutritional value and food properties biologically active additives (BAA) are used, which allow to optimize the composition, improve the nutritional value of foods and form their functional properties. Food additives production is a perspective direction, which can significantly extend the range of functional foods and products for special purposes.

Due to the fact that in Ukraine biologically active additives are produced in limited quantities, current market is filled with imported goods. In this regard, development of domestic production of new types of supplements from plant material is relevant and promising. Among them vitamins-multifunctional additives are of greatest interest that are complex multicomponent systems with certain properties. The use of plant material for purposeful to receive specialized products or natural food additives is very specific. By itself, the technology of their processing is quite complex, due to many factors, including the low acidity of raw materials and the need for mandatory and complete cleaning. Thus, wastes can reach more than 40%. A positive factor is the low cost of raw materials and predictable quality characteristics of the finished product [1, 2, 3].

We are interested in processing of carrots that are fruitful vegetable, widespread in many countries with good Agrobiological indicators and the possibility of long-term storage. Numerous authors are engaged technologies on processing carrots in BAA. Some of them have shown the feasibility of using carrots for creating a carotenoid additives radioprotective action, developed a scientific basis for their use in food technology and proposed development of pasty carotenoid additives. Others investigated possibility of preserving carotenoids during drying of raw carrot were made [1, 2, 3, 4, 5, 6].

Historically, national cuisines of many countries use extensively carrots. The main reason of popularity is not so expect color and strong taste, as its properties due to the presence of biologically active substances (BAS). Pectin, dietary fiber and natural carotenoid complexes are especially valuable, which have high stability, resistance to process and physiological activity. Of great importance  $\beta$ -carotene, which expect properties of provitamins has also an antioxidant, allows to improve the quality of the finished product and to continue its shelf life [7, 8, 9, 10, 11].

The aim of the study was to develop new technological solutions to better utilization of the properties of carrot to obtain two multifunctional dietary supplements containing carotene in dry and liquid form.

## Materials and methods

The object of research is the technology supplements containing carotene from carrots.

The subject of the research is to change the content of  $\beta$ -carotene during the processing of raw carrot in various ways. Materials of research is carrot varieties Shantanu 2461, carrot juice, husks, powdery Enrichment from carrot husks containing carotene and concentrated liquid filler containing carotene.

Raw materials, materials, semi-finished and finished products were characterized using a range of modern physico-chemical, chemical, microbiological, organoleptic and mathematical methods.

Contents of dry substances,  $\beta$ -carotene, sugars, fiber and pectin were determined according to the international standards ( ISO 751:1998(en), ISO 750:1998(en), ISO 6558-2:1992(en), ISO 2173:2003(en).

For the detection the characteristic absorption bands of  $\beta$ -carotene in the studied samples - carrots, natural carrot juice and concentrated, fresh carrot husks and dried in various ways, were recorded in the range of samples cyclohexane; as the comparing solution using cyclohexane, in the

wavelength range of 200-800 nm, thickness 1 cm; measurement error wavelengths on a spectrophotometer (Cary 100 Scan UV-visible spectrophotometer) according to the passport data is  $\pm 1$  nm value of a point was 0.0001.

Husks, received after pressing, drying sent by one of the methods were convection, infrared and microwave drying. Drying husks were carried out before the final moisture 6, 5% of the layer thickness of 0,9-1,1 cm.

During the convective drying temperature husks drying agent (air) was 70°S, speed was 2.0 m / s, the drying period was 160 min.

When infrared drying the duplex IR heating husks was carried. As generators of infrared radiation tubular electric heaters (TEHs) were used. Thus electric heaters warming up was carried out at a value of exposure (E) 3660 W / m<sup>2</sup> for 5-10 minutes. Then the value of E for 30 min, gradually decreased to 1600 W / m<sup>2</sup>, and left unchanged until the end of the drying process. Adjusting the value of E, in the dry husks, the change of voltage that is supplied to the heaters was performed. Thus the same voltage was changed as follows: from 220 to 120 on the lower TEH and 100 B was changed at the top. Drying time was 75 min.

Investigation of the process dry husks was conducted on at the semigenerating facility "Artemis" with a frequency of 2540 MHz. Drying of the samples occurred in the pulse-periodic mode with interval 1 to 2 minutes at a value of the heat flux of 300 W / cm<sup>2</sup>. Drying time is 14 minutes.

## Results and discussion

To implement the project it was necessary to first analyze the distribution of carotenoids carrot in solid and liquid phase (fig. 1). To provide a semi-finished needed technological parameters was necessary to minimize sugar content in carrot husks Figure 1 shows the absorption spectra of molecules  $\beta$ -carotene in fresh carrots, carrot husks and natural carrot juice.

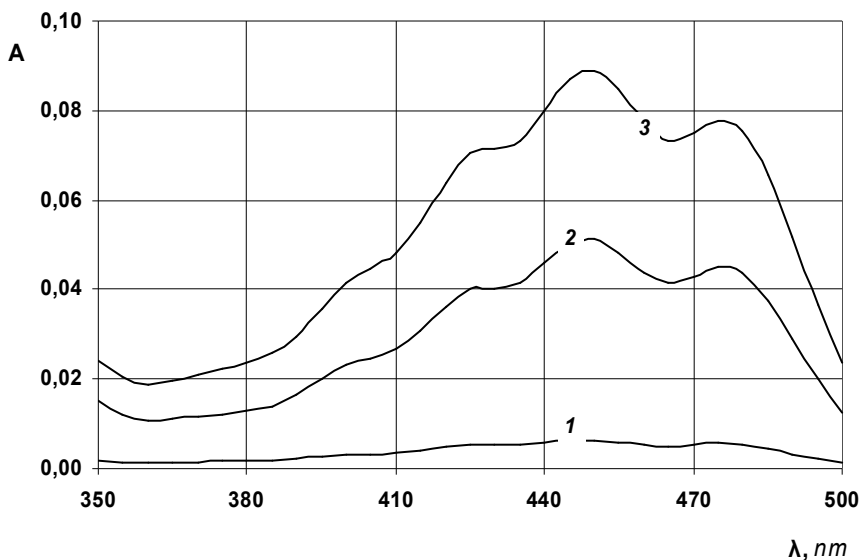
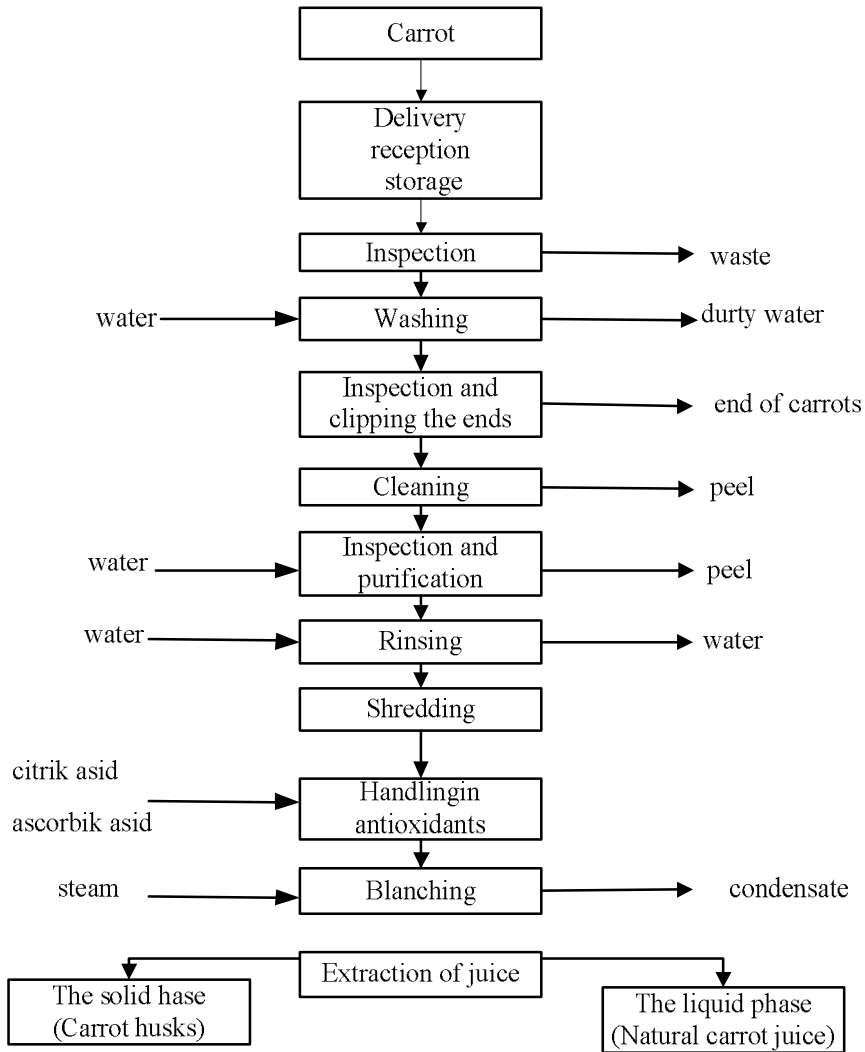


Fig. 1. Absorption spectra of molecules  $\beta$ -carotene:  
1 – carrot, 2 – carrot husks, 3 – natural carrot juice

— *Food Technologies* —



**Fig. 2 The principal technological scheme of processing carrots**

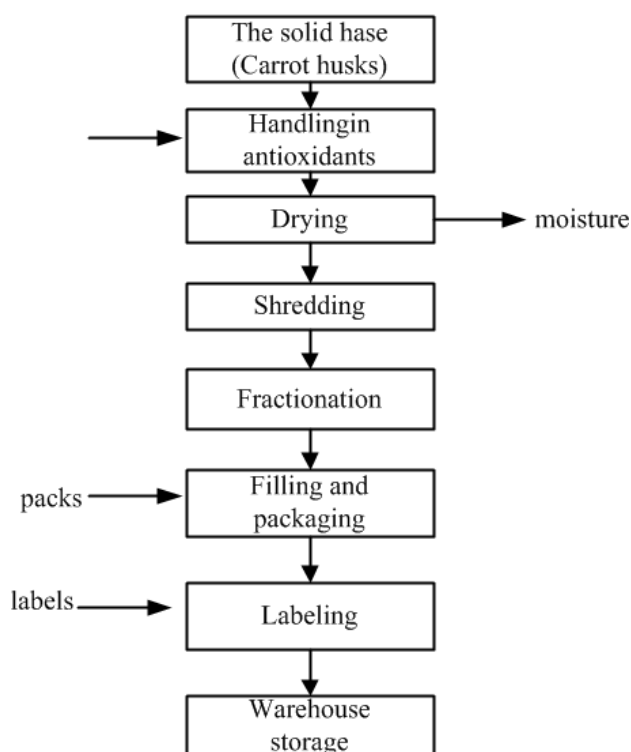
Figure 1 shows that the carotene content of husks, is 9,5 times greater than the natural carrot juice, which coincides with the research of many authors [10, 11].

Analysis of the known technologies of carrot allowed to reveal their "weak points" that adversely affect the quality of the finished product. Thus, the critical points in its processing is oxidation coloring substances and BAS during the grinding, pressing and drying. A key role in this complex is played by own enzymes carrots, the most active of which is peroxidase. Its inactivation is often a difficult task and requires special additional impacts on materials. Considering the fact that the enzyme activity is dependent on temperature, presence of atmospheric oxygen and pH, made a number of relevant research, that allowed to establish rational regimes of technological process of processing fresh



carrots, and its distribution on the solid and liquid phases. On the basis of research and optimization of individual technological modes it was suggested a complex resource saving processing technology of carrot for obtaining two basic products - dry enricher "Carrotynka" containing carotene obtained from carrot husks and liquid filler "Carrot honey", containing carotene obtained from carrots juice. The principal technological scheme of processing of carrots is shown in Figures 2.

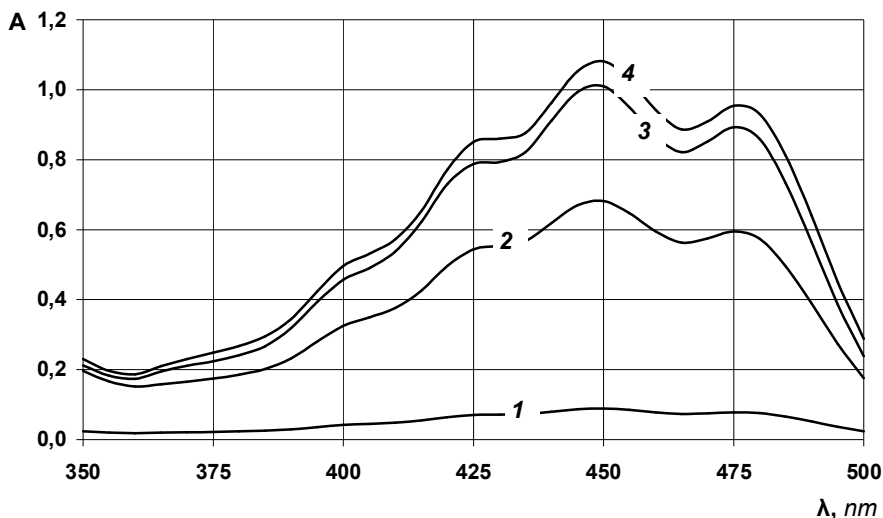
The essence of this technology comes down to the fact that the prepared carrot (washed and peeled) are ground in the crusher treated with complex antioxidants, followed by 5-10 minutes sharp pair and sent for pressing. So, the distribution of the product on the solid and liquid phases is made. The solid phase with the initial dry matter content (15%) after additional processing dried in various ways (convection, infrared radiation, in the microwave field) to 6-7% moisture content, crushed and packed (Figure 3).



**Fig. 3. The principal technological scheme production of dry carotene enricher "Carrotynka"**

The study of different methods carrot pomace drying proved the microwave method feasibility (Figure 4).

Thus, during the field of microwave drying  $\beta$ -carotene content decreased to 5,1% and pectin 4,3% on their original content.



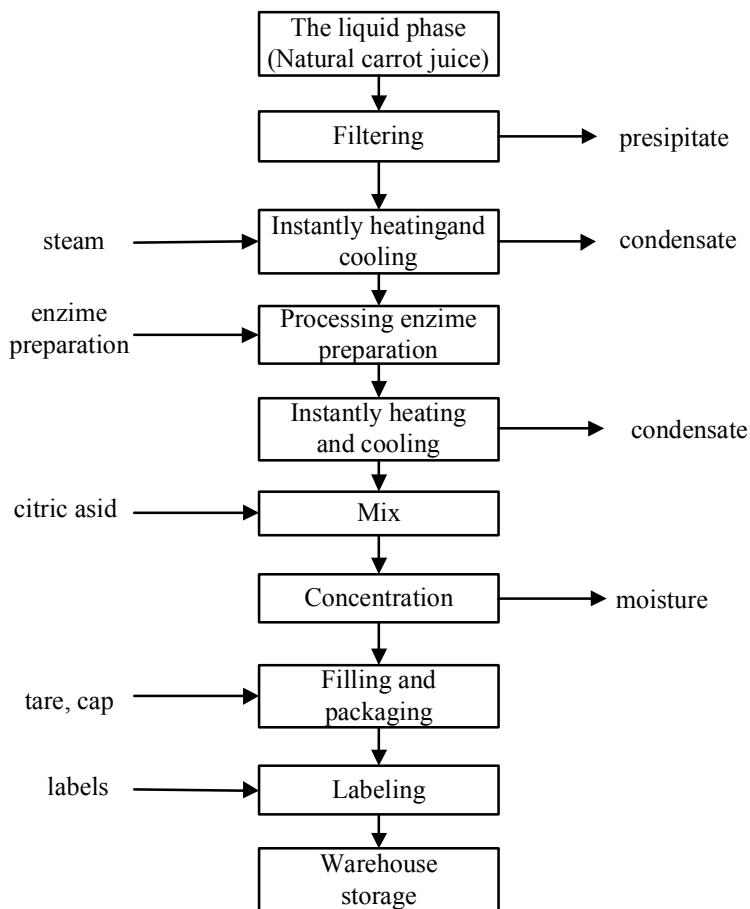
**Fig. 4. Absorption spectra of molecules  $\beta$ -carotene in powders obtained by different methods:**  
 1 - raw husks, 2 - dried convective way,  
 3 - dried IR radiation, 4 - in the microwave field.

The liquid phase (a natural carrot juice) after additional processing of enzyme preparation was concentrated to a solids content of 70% (Figure 5). The obtaining concentrated carrot juice differed strongly by strong orange color, high in  $\beta$  - carotene and pectin. During the concentration of carrot juice  $\beta$ -carotene content decreased to 7,6% and pectin – 8,5%, respectively.

Thus, in of the proposed technology it was got two products that can be used as multifunctional food additives. The comparative characteristic of some indicators of the chemical composition of carrot, semi-finished and finished products (derived food additives) are presented in Table 1.

**Table 1**  
**Organoleptic and physico-chemical parameters dry carotene enricher "Carrotynka" and concentrated filler containing carotene "Carrot honey"**

Parameters	Carrotynka	Carrot honey
<b>Organoleptic parameters</b>		
Appearance	The powder is homogeneous on all bulk	Opaque the viscous liquid
Taste	A natural inherent carrots	Natural, close to natural carrot juice
Flavor	Orange	Dark orange
<b>Physicochemical parameters</b>		
Contents of dry substances,%	93,0-94,0	70,0-75,0
Contents of carotene,mg/100g	148,0-154,0	11,0-12,0
Content of pectin, g/100g	5,0-6,0	3,0-3,5
Content of sugars, g/100g	7,0-8,0	45,0-55,0
Content of fiber foods, mg/100g	20,0-24,0	-



**Fig. 5 The principal technological scheme production of concentrated filler containing carotene " Carrot honey "**

An enrichment "Carrotynka" received in a production environment by microwave drying, has got a high content of  $\beta$ -carotene (148-154 mg/100 g) and fiber foods 20-24 (mg/100 g), and filler "Carrot honey" (70% solids) - rich in sugars (45-55 g/100 g),  $\beta$ -carotene (up to 11 mg/100 g) and pectin (up to 3,5 g/100 g).

Obtained additives should be stored in vacuum packaging avoid light at temperatures below 5°C. Loss carotene is 20-25%. The total number of microorganisms during storage is not increased.

Assessing quality index and technological properties of the obtained products, they were subjected to various technological influences. As a result of these tests it can be noted a relatively high stability of obtained food additives to various modes of process and be recommend them for wide use in food technology as a multifunctional enriching additives.

We had tested a number of technologies of getting canned products from restored carrot juice, as well as development of confectionery and bakery products of new recipes, which gave a positive result.

## Conclusion

1. Developed the technology a complex processing carrots with production dry carotene enricher "Carrotynka" and concentrated filler containing carotene "Carrot honey".
2. Blanching carrot in the pair atmosphere and treatment with antioxidants, which provides peroxidase inactivation by 85%, saving  $\beta$  - carotene by 95%, Vitamin C - 75% and sugar - 93%.
3. To prevent the loss of  $\beta$ -carotene, coloring agents and sugars in the drying process after grinding carrots and carrot husks before drying, they are treated with antioxidants.
4. The highest content of  $\beta$ -carotene – 148-154 mg / 100 g can be obtained by drying the carrot husks in the field of microwave.
5. The optimal method of storage additives it is vacuum packing without light and temperature below 5 °C.
6. The obtained products containing carotene, can be used in food technology as a multifunctional enriching additives.

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## Analysis of diffuse reflectance spectra of powdered milk and their relationship to technological parameters

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### Abstract

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**Introduction.** In order to improve products for baby food a research of animal milk has been conducted. The study of diffuse reflectance spectra of various food products makes it possible to determine the different physical and chemical characteristics.

**Materials and methods.** Infrared reflection spectra of powdered milk, which is recommended to be used in infant formulas, were tested using the device "Infrapid-61". Diffuse reflectance spectra of powdered milk products were studied within 1330-2370 nm in increments of 10 nm.

**Results and discussion.** The diffuse reflectance spectra of powdered milk of such domestic animals like goats, sheep and mares are quite similar, but at certain wavelengths there are significant differences. All the tested reflection spectra of mare and goat milk are similar in form. The reflection spectrum of sheep milk is slightly different from the previous ones. So at a wavelength of 1720 nm for all three spectra minimum reflection is observed, but in the spectrum of mare milk this extremum is considerably lower. Similar conclusions can be drawn by analyzing the spectra at wavelengths 2310 and 2350 nm. The special features include the fact that in the range of 2010-2220 nm wavelength reflection spectrum of mare milk is a monotonic curve with one extremum at a wavelength of 2110 nm. At the same time, the reflection spectra of sheep and goat milk show two extremes at wavelengths 2060 and 2170 nm. An important spectral range is within 1480-1500 nm wavelengths, which is responsible for the presence of protein in the samples. Especially low minimum characteristic of mare milk, that has the least amount of protein in its chemical composition, was confirmed by independent experiments. The protein content for goat and sheep powdered milk does not differ significantly. This conclusion is confirmed qualitatively, based on analyzes of reflection spectra.

**Conclusions.** The tests of diffuse reflectance spectra in the near infrared wavelength revealed significant differences in the wavelength division for goat, sheep and mare powdered milk and made it possible to carry out a qualitative analysis.

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## **Introduction**

The basis of dairy products for baby food, produced in Ukraine, is cow's milk, the components of which make undesirable impact on immature baby's body. That is why the cow milk prototyping is an urgent problem in the production of baby food. As a substitute for cow milk the milk of domestic animals - goats, sheep and mares was suggested to examine. Currently numerous infant formula are available, they are breast milk substitutes that are considered adapted to a baby's body. Yet, children who are deprived of breastfeeding and get bottle-feeding do not get the amount of natural nutrients, which is found in human milk. To balance the composition of adapted formula different blends of vegetable oils, vitamins, mineral complexes, etc. are added. No animal milk can be compared to human milk in its composition.

Recently the number of different allergic diseases among children is inclined to increase steadily. Clinical implications of allergic reactions, mainly related to dietary habits, can be observed from infancy. Food allergies of infants are mainly allergies to cow milk protein. Its prevalence among infants up to twelve months is not known with certainty, though, it is estimated 2 to 6%. Often the diagnosis is made based on the symptoms of skin rash, seborrhea, dermatitis, functional disorders of the digestive system, nasal breathing disorders, sleep disorders.

In order to improve products for baby food the studies of milk of such animals as goats, sheep and mares have been undertaken. Along with the standard methods of determination of substances infrared spectroscopy method has recently gained widespread use. This is due to the fact that this method gives the possibility of rapid, non-destructive analysis of substances using modern computer technology. Reflection spectra of various food has been studied by scientists from many countries for over a decade. However, the interesting features of infrared reflectance spectra of powdered milk offered to use in baby food have been revealed by us with the help of device "Infrapid-61." The study of diffuse reflectance spectra of various food products makes it possible to determine different physical and chemical properties: moisture, content of proteins, fats, sugars, starch and so on.

## **Materials and methods**

The object of the research were samples of powdered animal milk: goat, sheep and mare milk which is going to be used to improve baby food. This milk was received in semi spray dryer "Nyro-Atomizer" with a 0.9 m<sup>3</sup> working volume of camera and producing capacity of evaporated moisture up to 10 kg / h. Dryer makes it possible to ensure the temperature of the drying agent in the range 120 ... 250 ° C at the inlet of the dryer and 80 ... 100 ° C at the outlet. Recently, along with the standard methods of determination of substances the method of infrared spectroscopy gained widespread use, particularly in the near infrared wavelength. Therefore, to study samples of powdered milk products the device "Infrapid-61" operating in the wavelength range 1330-2370 nm was used.

Automatic measurement of reflectivity in this wavelength was performed in increments of 10 nm, allowing us to obtain diffuse reflection spectra of different kinds of powdered milk products. Thus there was no need of special sample preparation because it had a homogeneous structure. Therefore, samples were kept under the same conditions with low humidity, directly loaded into sample compartment and analyzed within a few minutes. Another feature of this method is that it does not require special chemicals sample preparation.

The chemical composition of these products was determined by standard methods. Mass fraction of protein was determined by turbidimetric method. The method is based on measuring the luminous intensity of scattered solid or colloidal particles that are suspended in solution. The intensity of light scattering, defined by turbidimeter, informs us about the concentration of the substance.

For the experiment, 0.5 g of the product must be weighed within the accuracy to 0.001 g in a conical flask of 250 cm<sup>3</sup>. Add 50 cm<sup>3</sup> burette 0.05 mol / dm<sup>3</sup> sodium hydroxide solution. Close the flask with a stopper and shake for 15 minutes in mechanical shakers. 10 minutes is necessary to centrifuge (speed 6000 min<sup>-1</sup>), followed by 5 cm<sup>3</sup> of centrifugate dispensed with pipette into a volumetric flask of 50 cm<sup>3</sup>. Fill up the contents of the flask to the mark with sulfosalicylic acid. The flask is to be quickly flipped 2-3 times and the solution poured into sample compartments with a layer thickness of 5 mm. Measure for Optical density (wavelength 550 nm). Mass fraction of protein is determined by the calibration curve. Making the calibration curve - to make the calibration curve we select samples with different mass fraction of protein in the range that occur naturally (8 to 20%). Range interval in protein content of samples must be within 1%. The number of samples should not be less than 10. Accuracy of values increases with sample's number.

Mass fraction of lactose in milk was determined by iodometric method. The gist of the iodometric method of determining lactose is as follows. Known amount of copper sulfate (CuSO<sub>4</sub>) in excess is added to a known quantity of milk with unknown concentration of lactose. Part of the copper is used for lactose oxidation and the other part remains unchanged in divalent state. This reaction takes place in an alkaline environment that is created by adding alkali (NaOH). We do not know yet the amount of copper that has reacted with lactose. To calculate it, the known volume of solution of iodine (I<sub>2</sub>) and sodium hydroxide (NaOH) is added to the mixture. As a result we get two compounds - sodium iodide and iodate (NaI and NaIO<sub>3</sub>). Copper, which does not enter in reaction with lactose, reacts with sodium iodide (NaI), resulting in the formation of molecular iodine (I<sub>2</sub>), which again goes into ionic state after reaction with sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). The dose of thiosulfate solution is proportional to the dose of molecular iodine, which was formed, and to the dose of bivalent copper, which did not react with lactose. Since the initial volume of the solution of copper sulfate and its concentration is known, the calculations set amount of copper, which came in reaction of lactose oxidation, and then the content of the lactose in milk.

For the experiment, 25 g of milk must be weighed within the accuracy to 0.01 g in a volumetric flask of 500 cm<sup>3</sup>. Add distilled water to half the volume of the flask. Then add 10 cm<sup>3</sup> of solution CuSO<sub>4</sub> (Fehling reagent I) with a pipette. Add 4 cm<sup>3</sup> of 1 mol / dm<sup>3</sup> sodium hydroxide (NaOH) with pipette. Stir the mixture and fill up the substance of the flask to the mark with distilled water. Stir and leave still for 30 minutes. The liquid is filtered through a filter paper (the first 10 ... 20 cm<sup>3</sup> of filtrate is extracted). Proceed to filter into a dry flask. 50 cm<sup>3</sup> of the filtrate is measured with a pipette and put into a conical flask of 250 cm<sup>3</sup>. Add 25 cm<sup>3</sup> of 0.1 mol / dm<sup>3</sup> solution of iodine (I<sub>2</sub>) with a pipette. Slowly add 37.5 cm<sup>3</sup> of 0.1 mol / dm<sup>3</sup> sodium hydroxide (NaOH), and constantly stir the substance of the flask. The flask is closed with a stopper and left in the dark for 20 minutes. Add 8 cm<sup>3</sup> 0.5 mol / dm<sup>3</sup> of hydrochloric acid (HCl) from a cylinder, and at this moment we can observe allocation of molecular iodine. Disengaged iodine is immediately titrated by 0.1 mol / dm<sup>3</sup> of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) to the appearance of straw yellow color. Add 1...2 cm<sup>3</sup> of 1% starch solution; at this mixture color turns dark blue due to the reaction of starch and iodine. Continue adding sodium thiosulfate until the discoloration of the mixture,



which will be held using 1...2 extra drops of thiosulfate. Record total volume of sodium thiosulfate, which was used for titration,  $\text{cm}^3$ .

Next, the control experiment is held. Instead of the filtrate  $50 \text{ cm}^3$  of distilled water is measured into a flask and the experiment is performed in the same way and with the same reagents as in the main experiment, starting with putting  $50 \text{ cm}^3$  of the filtrate into a conical flask of  $250 \text{ cm}^3$ .

Mass fraction of lactose  $L$  (%) is calculated by the formula:

$$L = \frac{0,01801 \cdot (V_1 - V) \cdot 100 \cdot 0,97}{m}, \quad (1)$$

where  $0.01801$  is the amount of lactose corresponding to  $1 \text{ cm}^3$  of  $0.1 \text{ mol} / \text{dm}^3$  iodine solution, g;

$V_1$  is the amount of  $0.1 \text{ mol}/\text{dm}^3$  solution of  $\text{Na}_2\text{S}_2\text{O}_3$  which was spent on the titration of iodine in the control experiment,  $\text{cm}^3$ ;

$V$  is the amount of  $0.1 \text{ mol}/\text{dm}^3$  solution of  $\text{Na}_2\text{S}_2\text{O}_3$  which was spent on the titration of excess iodine in the filtrate,  $\text{cm}^3$ ;

$0.97$  is the amendment established empirically;

$m$  is the mass of milk in  $50 \text{ cm}^3$  of filtrate, g

Fat content in milk was determined by acid method. The method is based on milk fat separation under the action of concentrated sulfuric acid and isoamyl alcohol, followed by centrifugation and measuring the amount of fat released in the graded part of butyrometer.  $10 \text{ cm}^3$  of sulfuric acid is poured into two milk butyrometers (1-6, 1-7) with a dispenser, and carefully so the liquids do not mix add  $10.77 \text{ cm}^3$  of milk with a pipette.  $1 \text{ cm}^3$  of isoamyl alcohol is added to each butyrometer with a dispenser. Butyrometers are closed with dry plugs. Butyrometers are shaken until proteins get dissolved, turning them at least 5 times, so that the liquids are completely mixed up inside. Butyrometers are set on a boiling-water bath for 5 minutes at  $65 \pm 2 \text{ }^\circ\text{C}$ . Taken off the bath, butyrometers are put in centrifuge cups with their graduated parts down. Butyrometers are placed symmetrically opposite each other. They are centrifuged for 5 min. Each butyrometer is removed out of the centrifuge, and by moving rubber stoppers regulate fat rod so that to keep it in the graded part of butyrometer. Butyrometers are put on a boiling-water bath at  $(65 \pm 2) \text{ }^\circ\text{C}$  with their stoppers down for 5 minutes, when the water level in the bath should be somewhat higher than fat level in the butyrometer. Butyrometers are taken out one by one and then calculation of fat is made immediately. To analyze the reconstituted milk it undergoes heating up on a boiling-water bath at  $(65 \pm 2) \text{ }^\circ\text{C}$  for 5 min three times between each centrifugation. Butyrometer indicators show mass fraction of fat in milk.

## Results and Discussion

After milk research was made we received the data given in Table 1.

The results obtained by infrared spectroscopy given in Figure 1 showed that the diffuse reflectance spectra of powdered milk of animals such as goats, sheep and mares are similar in nature, but at certain wavelengths there are significant differences.

Table 1

Composition of powdered animal milk			
Milk	Protein mass fraction, %	Fat content, %	Mass fraction of lactose, %
Sheep	25,2	32,0	21
Goat	29,6	22,0	40,0
Mare	16,1	12,0	66,0

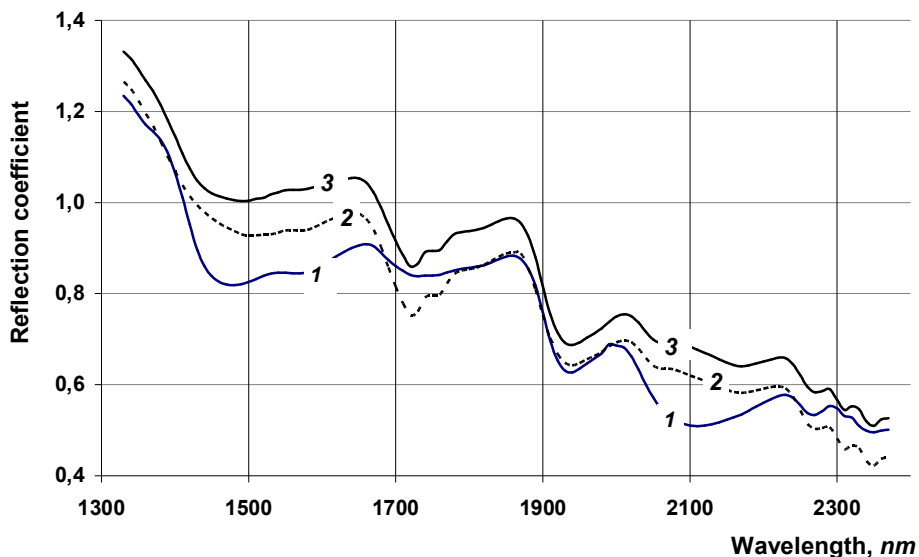


Figure 1. Reflection spectra of powdered animal milk:  
1 – mare; 2 – sheep; 3 – goat.

Comparative analysis of the diffuse reflectance spectra of powdered milk samples showed that all the tested reflection spectra of mare and goat milk are similar in form. It should be emphasized that the reflection spectrum of sheep milk is slightly different from the previous ones. So at a wavelength of 1720 nm for all three spectra minimum reflection is observed, but in the spectrum of mare milk this extremum is considerably lower. Similar conclusions can be drawn by analyzing the spectra at wavelengths 2310 and 2350 nm. The special features include the fact that in the range of 2010-2220 nm wavelength reflection spectrum of mare milk is a monotonic curve with one extremum at a wavelength of 2110 nm. At the same time, the reflection spectra of sheep and goat milk show two extremes at wavelengths 2060 and 2170 nm, respectively.

An important spectral range is within 1480-1500 nm wavelengths, which is responsible for the presence of protein in the samples. Especially low minimum characteristic of mare milk, that has the least amount of protein in its chemical composition, was confirmed by independent experiments. As for the goat and sheep powdered milk, the protein content of these products does not differ significantly. This conclusion is confirmed qualitatively, based on analyzes of reflection spectra. Interesting results were obtained

using electrophoresis in the study of protein fractions of the samples. It was found that proteins of goat and sheep milk contain different amounts of casein in its composition. This fact may explain some differences in reflectivity coefficients of goat and sheep milk for this range of wavelengths. In the spectral range 1930-1950 nm the coefficients of reflectivity samples are close. This range of wavelengths characterizes humidity of any food product. It should be mentioned that powdered milk was obtained for baby food production. Therefore, it imposed more stringent requirements for moisture content, which should not exceed 4% in such product. Product moisture control can be easily carried out, using quantitative analysis by NIR spectroscopy. Interestingly, the spectral distribution at a wavelength of 2110 nm mare milk reports a deep minimum, confirming the low content of casein and protein. The comparative analysis in this part of the spectrum again confirms the fact that the mare milk contains much less protein and casein (1.5-2 times) compared to sheep and goat milk. Noteworthy is the wavelength of 2350 nm, where there is minimum reflection for all three samples. This wavelength carries some information about the content of fat in the product. It should be noted that, according to previously obtained data, the fat content in sheep milk is the biggest, quantitative content of fatty acids in sheep milk is quite different from the content of some fatty acids in mare and goat milk.

## Conclusions

The research of diffuse reflectance spectra in the near infrared wavelength revealed significant differences in the spectral distribution for goat, sheep and mare milk and made it possible to carry out a qualitative analysis. It was found out that these studies enable us to analyze the composition of the products, or to identify similarities and differences of the samples. Diffuse spectroscopy method provides a comparative analysis of the products, but requires significantly less time to get results than the methods determining each indicator in the products.

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## The sour milk drink with antioxidant properties

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### Abstract

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**Introduction.** The use of pectin and a P-vitamin complex, isolated from green tea, as functional ingredients of sour milk drinks will expand the range, improve the consistence of the finished product and it will increase its nutritional value.

**Materials and methods.** The evaluation of taste and smell of the sour milk drink was performed using the profile method, based on the fact, that individual impulses of taste and smell, if they unite, give a quality new impulse of the common taste and aroma characteristics of the product. The study of structural and mechanical properties of the samples were performed on the viscometer "Reotest 2". The organoleptic indices of drinks were evaluated using a five-point scale for assessment the expressiveness of the relevant sample.

**Results and discussion.** The best profile for all considered characteristics belonged to the sample of sour milk drink with citrus pectin. It is characterized as harmonious, sour milk, refreshing drink with pronounced citrus scent. Based on the researches and on the study of the rheological properties of samples of sour milk drinks, it was found, that they belong to coagulatory structures. The analysis of measured rheological characteristics showed, that the investigated samples with P-vitamin complex belong to the structured solid body with the highest strength of structured bonds, also they have such characteristic, as thixotropy. The strongest structured framework is observed in the sample, containing fruit pectin and P-vitamin complex and containing citrus pectin. Rheological properties of soulmilk clots that is got at optimal terms were prospected. It is set that maximal effective viscosity of clots due to pectin substances and antihunt and P-vitamin complex rises, comparatively with control, in 2,08 and 1,76 times.

**Conclusions.** It is shown, that the use of fruit pectin with P-vitamin complex improves a texture and a structure of the sour milk product, and the descriptors of taste and smell are showed up better.

## Introduction

Milk drinks are very popular among people in the products of functional purpose due to its refreshing taste, delicate texture and beneficial effect on the human body. A variety of dairy products depends not only on the type of yeast, but on the injection of enriched food supplements.

The selection of enrichers dairy drinks should consider the features of microstructure, rheological properties and biological compatibility of enricher's components and milk-based product. Expanding the range of dairy drinks with functional purpose reveals the possibility of enriching them by biologically active substances, which are a deficiency in the diet of modern man.

Vitamin P is enough spread in nature and located in the hips, black currant, mountain ash, citrus, grapes, green tea leaves and buckwheat; various flowers in a free state or in the form of glycosides. Especially catechins have high P-vitamin activity, which belong to bioflavonoids. Vitamin P shows antioxidant properties, strengthens capillary walls and increases resistance of tissue to radiation damages [5]. The use of pectin in sour milk industry as a stabilizer of consistency opens up opportunities to create a fully qualitative food [6]. Use of pectin and P-vitamin complex isolated from green tea as functional ingredients of dairy drinks will extend the variety, improve the consistency of the finished product and increase its nutritional value of course [16-19, 21-23].

The purpose of research is to study the organoleptic and rheological properties of sour milk drink with P-vitamin activity.

## Materials and methods

During the technological processes of milk drinks receiving (milk-based of domestic production with 2.6% fat) it was held the following operations: fermenting milk (which firstly was boiling) in pH 4.0° C temperature with simultaneous application of dry leaven such as "Symbiotyk" and TM GoodFood and P vitamin complex with relevant pectin (fruit or citrus), and then thoroughly mixing this mix. Further ripening was conducted at 18° C for 24 hours in aerobic environment. Calculation was held for 100g of milk.

The obtained investigated samples consist of the following components: 1 - contains only milk ferment and dry leaven; 2 - milk, dry leaven and ferment fruit pectin; 3 - milk, dry leaven and citrus pectin; 4 - milk, dry leaven and P-vitamin complex, 5 - milk, dry leaven, P-complex vitamins and fruit pectin, 6 - milk, dry leaven, P-vitamin complex and citrus pectin.

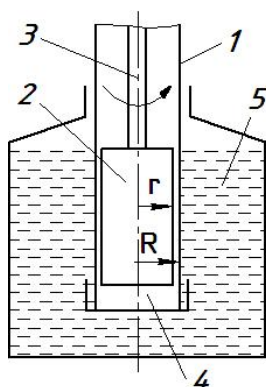


Fig. 1. Chart of device "Rheotest - 2"

The study of structural and mechanical properties of the samples were performed on viscometer [4, 24]. Viscosity measurements were carried out using the device "Rheotest-2", which operates on a constant shear rate.

1. Prepare a sample of 100 cubic centimeters of the set system, mix her and maintain 20-30 minutes.
2. In the immobile external cylinder of device 1 (Fig. 1) inundate 30-40 cm<sup>3</sup> of the investigated system.
3. Put an internal cylinder 2 on an axis 3 that is connected with an electric engine.
4. An external cylinder 1 with the structured system is put on the fixed internal cylinder 2 and lift to support.
5. Fix position of external cylinder by means of nut. The investigated system is evenly distributed in a gap 4

between coaxial cylinders (external 1 and internal 2). If necessary the system is maintained in a thermostat 5 at a certain temperature (Fig. 1)

6. On condition of permanent tension of change  $P = \text{const}$  to the internal cylinder deformations (12 or 24) give certain permanent speed, here an external cylinder stays still.
7. Register velocity of circulation of movable cylinder 2 by means of potentiometer. Velocity of circulation of cylinder is proportional to speed of deformation of the investigated system.
8. Tensions of change of  $P$  expect, that arises up in the system, after equalization:

$$P = z \cdot \alpha$$

$Z$  - became internal cylinder (driven to the passport of device, for example, for the cylinder of S2 -  $Z=5,39$  Pa);  $\alpha$  - it is a value of scale on an indicatory device (potentiometer).

9. The values of gradients of deformation  $\dot{\epsilon}$  for every velocity of circulation (12 values) take from passport data.
10. After the values of tension of change of  $P$  and gradient of deformation  $\dot{\epsilon}$  expect dynamic viscosity  $\eta$ :

$$\eta = \frac{P}{\dot{\epsilon}}$$

$\eta$  - dynamic viscosity, Pa·s;  $P$  - is tension of change, Pa;  $\dot{\epsilon}$  - it is speed of change,  $s^{-1}$ .

11. The experimental data build complete rheological curves of viscosity  $\eta = f(P)$  and fluidity  $\dot{\epsilon} = f(P)$ .

The evaluation of taste and smell of the sour milk drink was performed using the profile method, based on the fact that if individual pulses of taste and smell are united, they will give a new pulse in the common taste and aromatic characteristics of the product. As a standard of comparison were used the sour milk leaven without filler, which determined the order of appearance and intensity of individual pulses [7, 9].

## Results and discussion

The organoleptic drinks were evaluated using a five-point scale to assess the conformity of the sample [7- 9]. During the organoleptic evaluation of sour milk drink was used a five-point scale:

- 5 stars - excellent quality
- 4 - good
- 3 - satisfactory,
- 2 - bad (defective food product)
- 1 - very bad (technical lack).

### *Main descriptors of taste:*

- 1 - strong sour milk flavor;
- 2 - sour and fruity;
- 3 - slightly sour taste;
- 4 - sour taste with a bitter taste;
- 5 - strong bitter taste;
- 6 - harmonious sour and bitter taste.

### *Main descriptors of smell:*

- 1 - pleasant;
- 2 - satisfactory;
- 3 - satisfactory;
- 4 - satisfactory;
- 5 - bad;
- 6 - bad.

Fig. 1, 2 shows profiles of taste and smell of sour milk drinks compared with sour milk leaven.

As can be seen from the diagram Fig. 1 and 2, during the injection of pectin and P-vitamin complex in a sour milk leaven (sample number 2, 3, 4, 5, 6) is observed an intense change of taste and smell of course. It is established that P-vitamin complex strengthens the bitter tasted and pectin decreases and gives more softened flavors (sample number 5, 6). Sweet taste is strengthened if fruit pectin is injected (sample number 2, 5), citrus pectin (sample number 3, 6) - provides more refreshing taste with a strong sour milk taste.

The most optimal profile from all of considered descriptors was received by sour milk drinks sample with citrus pectin (sample number 6). It is characterized like a harmonious, sour milk, refreshing with strong citrus smell.

It has been established what kind of structures they are: coagulation or condensation-crystallization (based on research and study of the rheological properties of sour milk drinks' samples). It was held the comparative analysis of other technological characteristics to develop the functional drink [10, 11].

Fig. 3 and 4 represents viscosity, structural and mechanical characteristics of the samples №1, 2 and 3 without P-vitamin complex, respectively.

The most sturdy structured frame of systems ( $P_m$ ) and a range of stresses ( $P_m/P_k1$ ), which holds the destruction of structures represented in the sample number 3, contains citrus pectin. The greatest viscosity of system with particularly no destroyed structure ( $\eta_0$ ) and the strength of the system formed by a supramolecular structure that characterizes the anomaly of viscosity ( $\eta_0-\eta_m$ ) represented in the sample number 2, contains fruit pectin. From Fig. 3 it can be seen that the greatest viscosity of the system with particularly destroyed structure ( $\eta_m$ ) is represented in the sample number 1.

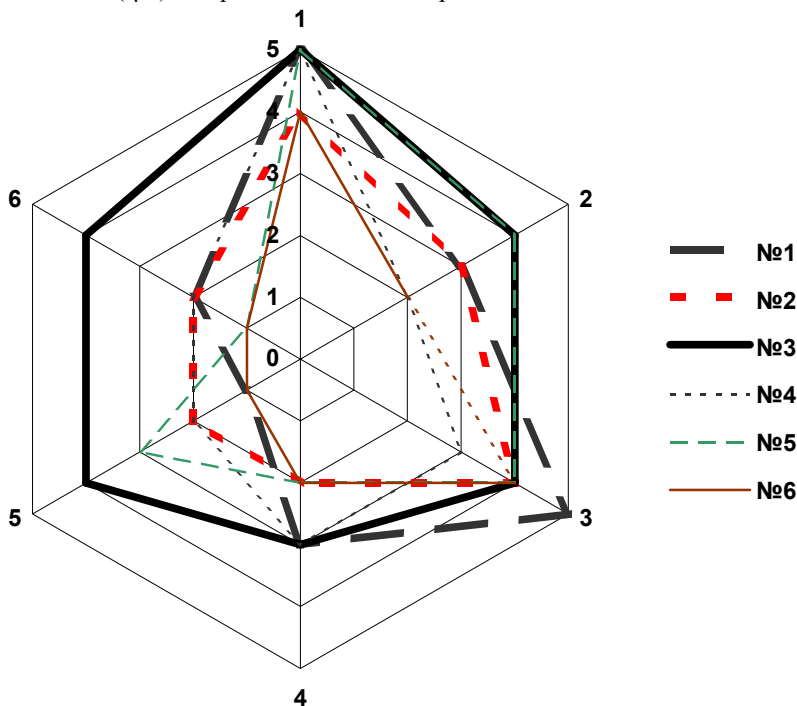
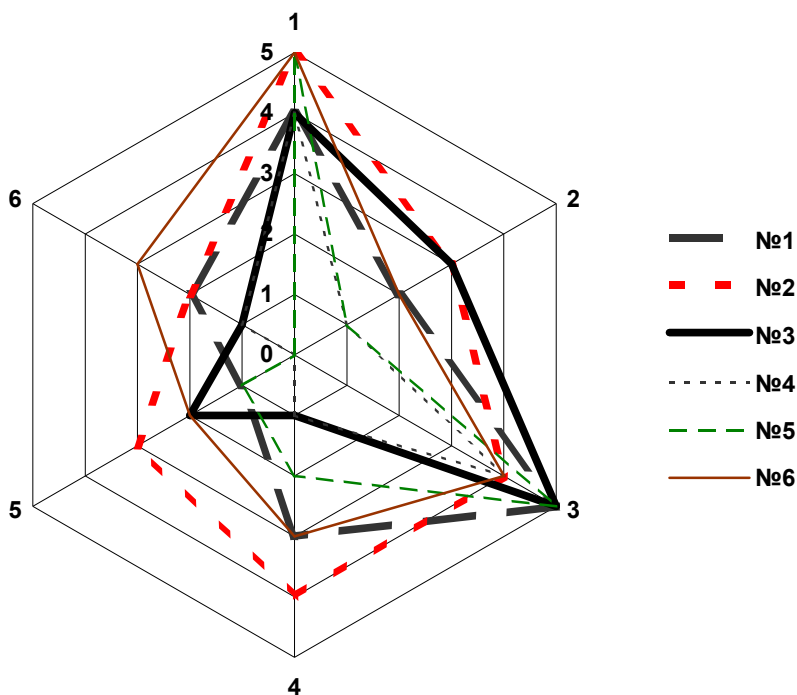


Fig. 1. The profile assessment of sour milk drink's flavor with pectin and P-vitamins





**Fig. 2. The profile assessment sour milk drink's smell with pectin and P-vitamins**

Viscosity, structural and mechanical characteristics of the samples number 4, 5 and 6 of the P-vitamins are shown in Fig. 5, 6. According to the results that are shown in Fig. 5, 6 the maximum values almost of all rheological parameters are represented in the sample number 5 containing fruit pectin and P-vitamin complex, only the lowest viscosity system with particularly destroyed structure ( $\eta_m$ ) is represented in the sample number 4 with P-vitamin complex.

After analyzing the rheological calculated parameters (Figure 6) it is shown that the investigated samples of pectin and P-vitamin complex belongs to structured solidlike body, have the greatest strength of structured bond and thixotropy. The most solid structured framework is observed in the sample number 5 containing fruit pectin and P-vitamin complex and in the sample № 6 with citrus pectin. The sample number 4, with only P vitamins, has the lowest viscosity system that confirm to particularly destroyed structure.

Rheological properties of soulmilk clots that is got at optimal terms were prospected. It is set that maximal effective viscosity of clots due to pectin substances and antihunt and P-vitamin complex rises, comparatively with control (a soul-milk product is without a pectin and P-vitamin complex), in 2,08 and 1,76 times for soulmilk clots with a fruit and citrus pectin. Next to the increase of viscosity in standards there is an increase of durability structural to framework. Tension of change is on the area of creep, that determines effort at that the system begins to collapse, at soul-milk clots in 2,43.2,53 times higher, than in.

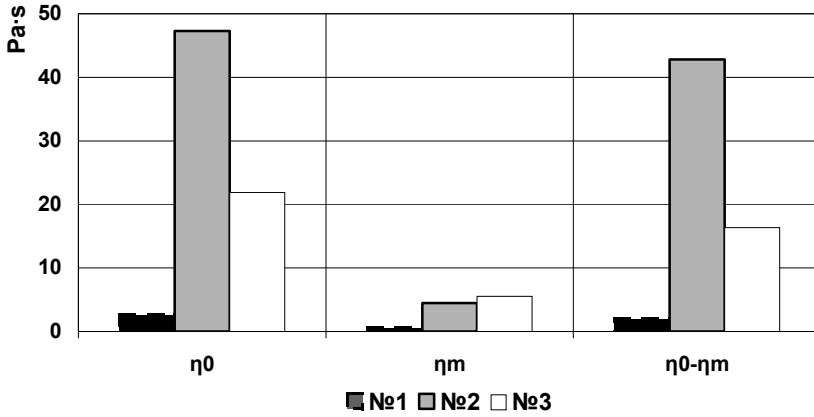


Fig.3. Viscosity characteristics of samples without P-vitamin complex

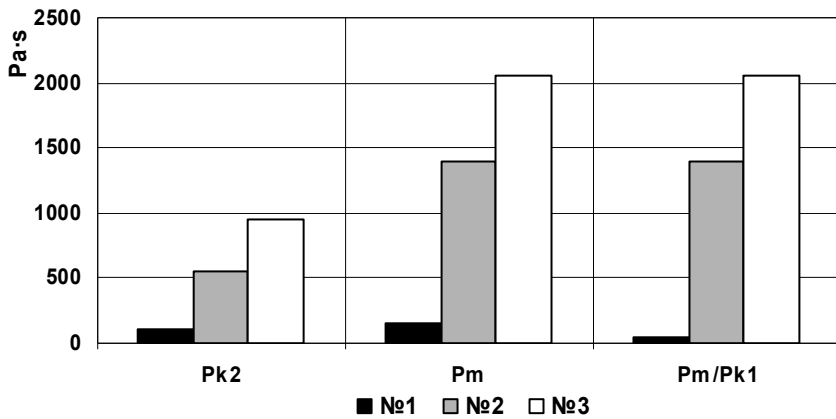


Fig.4. Structural and mechanical characteristics of samples without P-vitamin complex

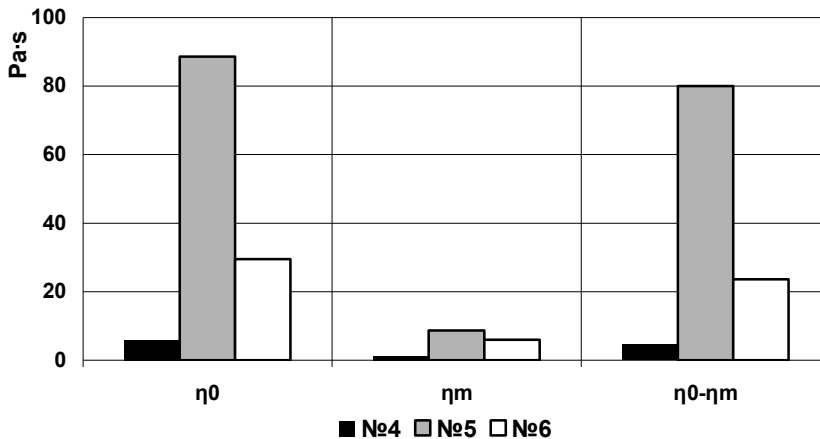


Fig.5. Viscosity characteristics of samples with P-vitamin complex

## Conclusions

The usage of P-vitamin complex as a functional ingredient for enriching sour milk drinks will expand their range and improve the nutritional and biological value.

It is shown that the usage of fruit pectin and vitamin P complex significantly improves the texture and structure of sour milk product and appear better taste and smell descriptors.

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## Using of polymers as carriers in encapsulation of spice oleoresins

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### Abstract

#### Keywords:

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**Introduction.** The general information about spice oleoresins, various polymers for encapsulation is generalized. Carrier system based on maltodextrin and silica is investigated.

**Materials and methods.** The materials of researches were encapsulated forms of oleoresin, rosemary and black pepper, encapsulated by mixture of maltodextrin and dioxin silicon. Was studied an influence of concentration of oleoresin in sausages on a change of their touch indicators and stability of microflora of boiled sausages using standard procedures.

**Results and discussion.** The overview of possible carriers of oleoresin was given in the article. Recent research findings on such carriers as carbohydrates, starches, maltodextrins, gums, proteins and other have been provided. Particular attention is paid to the advantages and disadvantages of each encapsulation system. The analysis of different combinations of polymers and their impact on effectiveness of encapsulation was given. It is described in short the investigation of carrier system based on maltodextrin and silica for encapsulation of oleoresins of rosemary and black pepper. Data are given about the bacteriostatic action of encapsulated forms of black pepper oleoresins and its combination with rosemary.

The "host-guest" complex of the black pepper oleoresin, which incapsulated in the mixture of maltodextrine (DE15-20) and silicium dioxide (A300) in the ratio 95:5 has been obtained. The shelf life of the boiled sausages has been increased twice in case of utilization of the "host-guest" complex in concentration of 0,2% to the forcemeat mass. The black pepper content in the boiled sausages was not exceed maximum allowable level (0,042%).

**Conclusions.** Even with an increase in the proportion of vegetable filler and the moisture in raw material encapsulated form oleoresins black pepper, and its combination with encapsulated rosemary oleoresins form during storage stabilized value of microflora is better than encapsulated form oleoresins of rosemary.

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## Introduction

Over the last decade, oleoresins successfully displace natural ground spices in food production due to significant advantages in application. Although most of the natural ground spices derived from tropical and subtropical materials have antioxidant properties, but they are also a source of microbial contamination, due to lesions of mold, mildew, damage by rodents and insects [1]. To achieve sterility it is necessary to pre-heat treatment which can lead to a loss of about 20% aromatics. As is generally known, the major part of the volatile fraction is bound and released by hydrolysis, for example, heat treatment of the meat products. However, since this process is not to end, the effective concentration of the volatile substances will always be less than the extracted oleoresins and extracts. Using ground spices of poor quality make blotches on the cut of the finished product possible, and that may not comply with the organoleptic characteristics with the current regulations [2].

## Literature review

The main components of oleoresins that are responsible for the aroma, flavor and color is volatile and nonvolatile materials fractions. This taste aromatic complex contains certain substances which remain composition of essential oils stable during the long storage term. Oleoresin is microbiologically sterile and has a bactericidal effect on the microbiome of the product to which they are attached [2].

The main oleoresin in meat market includes oleoresins of black pepper, allspice, white, nutmeg, mace, red pepper, cardamom and others. They may be of different essential oil content, type of solubility, degree of processing [1]. Due to the high concentration of active substances oleoresins are rarely used by direct application to the finished product, but applied on top of the carrier, which provides the most effective release of taste and flavor at a certain stage of production of food production [3].

Oleoresins have several disadvantages that complicate their use in food products. Under the influence of air, light, heat, water, they have a tendency to destruction and have a short shelf life in case of detention in inappropriate conditions. Thick and sticky consistency can cause a poor dispersion in the food matrix and processing. Mixed in food matrices, oleoresin shows a tendency to dry out and lose flavor because of the heat treatment [4].

Encapsulation prior to use oleoresins in food products is advantageous alternative solution for the purpose of limiting or reducing the aromatic and flavor degradation during processing or storage, simplifying use forms [4].

Encapsulation is a technique by which a single substance or mixture of substances contained within or covered with another substance or substances system. The covered substance is called base, active component or filler. And the covering materials are called encapsulating agent or carrier.

The purpose of encapsulation or coating of the active ingredient is to form a barrier between the active component and undesirable environment. Such a barrier would protect the active ingredient of light, oxygen and water, contacting with other substances [5]. Encapsulated oleoresins are protected from destruction and the loss of aromatics, and they also retain their stability for a long time. Additionally, in food processing or usage of oleoresins in powder form is more convenient. The encapsulation process of unstable substances consists of two phases. The first phase is the encapsulation of base with a thick solution of encapsulating material. The second one is cooling and drying the emulsion. Retention of aroma and taste is due to factors related to the chemical characteristics of the

basics features of encapsulating material, as well as the nature and parameters of the encapsulation technology. The stability of the matrices is important for the preservation of aromatics. Depending on the encapsulation process, the matrix may be of various shapes and structures, and various physical structures. It also affects the diffusion of flavoring substances and environmental factors, and stability of the food product during storage [6].

Criteria for selection of the encapsulating agent, mainly based on such physicochemical properties as solubility, molecular weight, melting point and crystallization, crystalline, viscosity, diffusion, film-forming and emulsifying properties. It also needs to take into account the commercially available materials and economic benefit [7].

Encapsulating material can be selected from a wide variety of natural and synthetic polymers depending on the intention and desired characteristics of the final product. First of all, the carrier should not exhibit reactivity with the base [5], well soluble in water, have a low viscosity at high concentrations [7], facilitate full release bases in any process, requiring dissolution [5], characterized by high emulsifying, stabilizing and film-forming properties, providing re-dispersion for the release of flavor with the given parameters of time and space [7]. Subsequently, the encapsulation efficiency and stability under different storage conditions, and degree of protection grounds are measured, and the surface of the microcapsules is investigated [5].

These properties are characteristic of many available materials, but most of them have limitations on use in the food industry. Today the most common carriers include proteins, gums, carbohydrates, waxes and mixtures thereof [7]. Each group has certain advantages and disadvantages. However, typical materials used for encapsulation include carbohydrates of low molecular weight, milk and soy proteins, gelatin, gum arabic, and several local substances such mesquite gum. However, there is still no single carrier or encapsulating substances which would be ideal for all required criteria. Therefore, in recent studies, more attention is given to the combination of encapsulating material such as encapsulating system.

Suitable carriers are such carbohydrates as starches, maltodextrin, solid sugar syrups are commonly used. The ability of these carriers in the binding of volatiles is complemented with their variety, a low price and spread use in food processes. Carbohydrates have a high solubility and exhibit low viscosity at high solids concentrations, but most of them are characterized by a lack of interfacial properties needed to increase the efficiency of encapsulation. For this reason, they are often combined with other encapsulating agents such as proteins or gums.

A new approach for improving the properties of certain carbohydrate encapsulating lies in their chemical modification. For example, certain modified starches having improved surfactant properties and is widely used in the encapsulation process. Binding volatiles treated starches are classified into two types. On the one hand it is well-known inclusion complexes wherein the flavoring component gets into the helical amylose ring through a hydrophobic message. On the other hand, there are the polar interactions which include hydrogenous connections between the groups of starches and aromatic substances are established [8]. The hydrolysis products of starch and maltodextrin are also capable of forming a matrix and provide high oxidative stability encapsulation oleoresins available in various molecular weightes have low viscosity in concentrated solutions and are in an advantageous position between cost and efficiency. The main disadvantages are the virtual absence of emulsifying properties and low level of volatile components [8]. However, studies have shown that certain flavoring can be retained maltodextrin DE figures 10 to 20. Pectin is a polymer that has the ability to form stable emulsions at low concentrations.

Emulsifying properties of pectin are due to the presence of residual protein in pectin connection. To prepare the stable emulsion pectin within 1-2% is sufficient.

Gum thickeners are usually soft and tasteless, but may affect the taste and aroma of the finished products. In most instances, the gum suppresses sweet taste significantly affecting the viscosity and preventing diffusion. Gum arabic is mainly used as an encapsulating substance due to its high solubility, low viscosity, emulsification and film forming properties and a high content of volatile components. It is believed that gum arabic is a versatile material for encapsulation. Gum arabic is preferred in the selection medium, since it is able to form with most oils stable emulsions over a broad range of pH values, and is ideal for encapsulating lipid droplets. However, its use in the food industry is limited by high cost, commercially available and ambiguous quality. Also, studies have found that the use of gum arabic as an encapsulating agent is ineffective for five monoterpenes.

Proteins are distinguishable functional properties such as solubility, viscosity, emulsification and film forming properties due to the presence of the amphiphilic properties, the ability to associate and interact with various types of substances. Proteins possess high binding properties for aromatic compounds. In the formation of the emulsion, the protein molecules rapidly are adsorbed on the surface of the newly formed fat-water section to provide physical stability of the emulsion during processing and storage. Milk, whey protein and gelatin are most widely used for protein encapsulation. In some cases, the use of whey protein helps to increase the encapsulation efficiency of up to 90% and also to provide high barrier antioxidant reactions.

However, the encapsulation capacity of whey protein concentrate (WPC) as compared to sodium casein is low. It was also investigated the effect of spray drying process on the physicochemical properties of the emulsion "oil in water", the stabilized milk proteins [5].

It was established that the spray drying process leads to denaturation and aggregation of  $\beta$ -lactoglobulin. By heat treatment of whey protein changes the functional properties of the dried powder, presumably due to thermal denaturation of proteins. Denaturation of proteins may occur when combining the two parameters, high temperature and high water activity. As a result, it is difficult to prevent the influence of the spray drying on the stability of formed powder.

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As a carrier serum proteins show the best results when combined with carbohydrates. In such systems, encapsulating they act as emulsifiers and film formers, whereas the carbohydrates serve as a material for forming the matrix [5].

Protein-based substances, so-called polypeptides, soy proteins or gelatin derivatives can form stable emulsions with volatile components. Nevertheless, their cold water solubility, the capability to react with carbonyl compounds and high price limit their alternative use as a carrier.

Gelatin hydrolysis product of collagen is widely used in coacervation encapsulation method. Adding a small amount of gelatin (1%) to a mixture of gum arabic and maltodextrin to an increase in the content of the active substance and formed on a surface of the hard crust.



## Materials and methods

The materials of researches were encapsulated forms of oleoresin, rosemary and black pepper, encapsulated by mixture of maltodextrin and dioxin silicon. Was studied an influence of concentration of oleoresin in sausages on a change of their touch indicators and stability of microflora of boiled sausages using standard procedures.

Touch indicators were rated on a scale of 1 to 5 like an average scoring.

The amount of tasters was 30 people.

The determination of microbiological indicators (content of MAFAnM) of boiled sausages was carried according to applicable regulations for this product group.

## Results and discussion

In all cases, the use of proteins as an encapsulating material, it should be noted that sometimes there are questions about the use of proteins as "coating material", due to their sensitivity to the parameter pH close to the isoelectric point. Moreover, often considered the religious and social issues (kosher food, vegetarianism) [7].

Due to the fact that one encapsulating agent cannot respond to the demands of all the criteria to the carrier, recent studies focus on alternative encapsulating matrices. Current tendencies in the formation of an effective carrier system are considered based on maltodextrin and silica. In this system, the silica acts as a surface modifier in the matrix encapsulation oleoresins.

As the modifier maltodextrins dioxin silicon - silica A300 (ORISIL 300) with a predominant size of up to 20 nm (60%) was used. As the carrier, a mixture of maltodextrin (DE15-20) and silica (A 300) in the ratio 95:5 were used as oleoresins oleoresins of rosemary and black pepper were used. Encapsulation of black pepper oleoresins on the carrier was in the ratio of 1:5. It corresponded to a standardized concentration of black pepper due to the indicators of regulatory. The composition of the formulation satisfies the version of Table 1.

**Table 1**

**Formulation composition of model sausages with black pepper and rosemary oleoresins**

<b>Sample №</b>	<b>C1</b>	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
Veal	30,0	30,0	30,0	30,0	30,0	30,0
Pork	30,0	30,0	30,0	30,0	30,0	30,0
Broilers' Red Meat	36,0	32,0	36,0	32,0	36,0	32,0
Salt	2,0	2,0	2,0	2,0	2,0	2,0
Rice Flour	4,0	8,0	4,0	8,0	4,0	8,0
Encapsulated form of Black Pepper Oleoresin	0,2	0,3	0,2	0,3	–	–
Encapsulated form of Rosemary Oleoresin	–	–	0,2	0,3	0,2	0,3
Water	30,0	40,0	30,0	40,0	30,0	40,0

The aim of the study was to identify an effective amount of making encapsulated oleoresins on model formulation for the evaluation of bacteriostatic stability of model sausages.

Data on changes in microbiological indicators of boiled sausages groups which were prepared by the formulations in Table 1 are shown in Table 2.

From Table 2 it can be seen that the samples exhibit greater stability obtained by the embodiments 3 and 4, in which the influences of oleoresins have associated.

**Table 2**  
**Microbiological data of model sausages during storage**

Sample	Total viable count, TVC, CFU/g	Value for 4 <sup>th</sup> storage day, TVC, CFU/g
C1	$1,0 \times 10^1$	$1,1 \times 10^3$
C2	$1,5 \times 10^3$	$7,0 \times 10^2$
C3	$3,0 \times 10^1$	$3,0 \times 10^2$
C4	$7,9 \times 10^2$	$2,0 \times 10^2$
C5	<10	$4,9 \times 10^2$
C6	$2,0 \times 10^1$	$1,3 \times 10^3$

Samples were detected bacteria of the colibacillus group (BCG), the presence of mold inoculation revealed a value of CFU / g is not more than 10 colonies per gram of product. At the beginning of storage, total viable count not exceed regulatory requirements. In the samples with a smaller share of chicken meat in the recipe, this relationship is more pronounced.

## Conclusions

Analysis of the literature has allowed to determine the effective carrier form for oleoresin encapsulation. Reliable data on the effective bacteriostatic action of encapsulated forms of black pepper oleoresins and its combination with rosemary have been obtained.

To identify the causes of such an effect must be more research communication water activity of sausage mass system, shape and concentration of encapsulated oleoresin on sausage mass.

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## Eduction of equilibrium state in vodkas by means of $^1\text{H}$ NMR spectroscopy

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### Abstract

#### Keywords:

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**Introduction.** The aim of work is to identify equilibrium state of hydroxyl proton of ethanol and water in various samples of vodkas and flavored vodkas produced in Ukraine, using  $^1\text{H}$  NMR spectroscopy.

**Materials and methods.** Volumetric pipette were used to set up a required volume (0,3 ml) of vodka or flavored vodka. External standard separated from testing substance which is required for LOCK's system operation deuterium solvent (acetone- $d_6$ ) of NMR's deuterium stabilization spectrometer is added into an ampoule in a special form capillary.  $^1\text{H}$  NMR spectra records and data processing were performed according to the instruction of FT-NMR Bruker Avance II spectrometer (400 MHz).

**Results and discussion.** Experimentally determined elements thermodynamic equilibrium of hydroxyl proton of ethanol and water in vodkas and flavored vodka, using  $^1\text{H}$  NMR spectroscopy. We set three groups of samples with equilibrium of hydroxyl protons of water and ethanol: unsteady; transitional; steady equilibrium.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of  $\text{EtOH}+\text{H}_2\text{O}$  ( $\delta_{\text{EtOH}+\text{H}_2\text{O}}=4,75\dots4,80$  ppm). Unsteady and transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of  $\text{EtOH}$  ( $\delta_{\text{EtOH}}=5,34$  ppm) and  $\text{H}_2\text{O}$  ( $\delta_{\text{H}_2\text{O}}=4,72\dots4,75$  ppm). Unsteady equilibrium is characterized by the presence of hydroxyl proton of ethanol ( $\text{EtOH}$ ), which is obvious. Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium.

**Conclusion.** The researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas and flavored vodkas. Equilibrium systems allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

## Introduction

NMR spectroscopy is widely used in physics research, industry, agriculture and other industries [1]. NMR plays a particularly important role in food chemistry where it is used in the study of both simple organic molecules and complex macromolecular structures and their complexes. A large number of articles discuss the use of NMR for research of food products; meat, fish, dairy products, vegetables, fruits, juices, pastry, cheese and alcohol products. This method provides comprehensive information with relatively simple obtaining spectra, thus greatly facilitating and accelerating chemical research.

NMR spectroscopy is most commonly applied to the nuclei of lightest isotope of hydrogen  $^1\text{H}$  (protium,  $^1\text{H}$  isotope) proton [2-4]. The spectra measured using such nuclei are called proton magnetic resonance (PMR) spectra. PMR accounts for about 90% of all research on NMR spectra. Most of them operate in the Fourier transform mode.

The principle of NMR spectroscopy is based on the magnetic properties of certain atomic nuclei that resonate in the radio frequency range of the electromagnetic spectrum when placed in a strong magnetic field at a certain magnetic field [1, 3-7]. This allows for the identification of nuclei in different chemical environments. This property is explained by the existence of nuclei with non-zero spin (intrinsic mechanical torque), that is determined by the sum of the spins of its constituent protons and neutrons [4-7]. The spin of the isotopes' nuclei with an even number of protons and an even number of neutrons is always equal to zero (zero moment). NMR is not observed in these nuclei [1, 7].

The first «low resolution»  $^1\text{H}$  NMR spectra of  $\text{H}_2\text{O}$  were obtained in 1946. The first «high resolution»  $^1\text{H}$  NMR spectra of  $\text{C}_2\text{H}_5\text{OH}$  were developed in 1951. At first glance, it may seem that these are fairly simple organic molecules, as many scientists [1, 4, 8-22] continue to conduct NMR spectroscopy of ethanol due to its relative simplicity.

At the same time NMR spectroscopy exhibits variations in characteristics of ethanol such as chemical shift, spin-spin interactions and the effect of chemical exchange [1, 11-14].

In accordance to the requirements of normative documents of Ukraine vodka - is an alcoholic drink with a strength of 37,5% to 56,0%, made of aqueous-alcoholic mixtures (AAM) processed by a special sorbents with or without volatile ingredients. Flavored vodka is an alcoholic drink with a strength of 37,5% to 56,0%, with a marked flavor and taste, prepared by processing AAM with a special sorbents with addition of non-volatile and volatile ingredients.

In the opinion of Hu N. and others [23] vodka is a fairly simple physicochemical system: a mixture of alcohol and water. However, each brand has its own distinctive taste and features on the molecular level. Research conducted by Hu N. and others [23] confirm that these differences are significant both during the stage of creating AAM, and in the final product - the commercial vodka. The major differences are associated with hydrogen bonds, in particular their strength, as confirmed by various research methods such as  $^1\text{H}$  NMR spectroscopy, FTIR spectroscopy, Raman spectroscopy.  $^1\text{H}$  NMR and FTIR spectroscopy demonstrates the presence of water in the hydrate structure  $\text{EtOH} \cdot (5,3 \pm 0,1) \text{H}_2\text{O}$ . Water can also be observed in AAM as well as in vodka. The authors [23] attribute this value with the perception of organoleptic characteristics of vodka.

Lots of attention in the work of Hu N. and others [23] has been given to  $^1\text{H}$  NMR spectra of hydroxyl proton of OH water and ethanol. Water protons are represented as narrow singlets with  $\delta_{\text{H}_2\text{O}} = 5$  ppm. The spectra of some samples are represented by the appearance of a second broadened OH signal of ethanol at a level of  $\delta_{\text{EtOH}} = 5,5$  ppm. The presence in the samples of a single signal of OH ethanol is attributed to the weak hydrogen bonds of ethanol.

The effect of impurities (such as salts, acids, phenols) strengthening the hydrogen bonds in AAM as well as in the finished product such as sake, has been studied by Nose et al. [24]. Hu N. and others [23] have identified that the impurity of compounds has an effect on the molecular dynamics in ethanol's hydration process.

Previously,  $^1\text{H}$  NMR research of AAM has been conducted and described in the work of Kuzmin O. et al [25-27]. The obtained results of this work have proved a fundamental difference in AAM behavior prepared from ethyl rectified spirit (ERS) and water that has been passed through a various processing. It is indicated by the presence of such features as divided signals of OH-protons of  $\text{H}_2\text{O}$  and EtOH, abnormal waveforms of  $\text{CH}_3$  and  $\text{CH}_2$ . Presence of these features characterize product with a lower tasting properties. In the contrary presence of combined signal of EtOH+ $\text{H}_2\text{O}$  and rational form of  $\text{CH}_3$  and  $\text{CH}_2$  signals (triplet - for  $\text{CH}_3$ , quartet - for  $\text{CH}_2$ ) - characterizes AAM with the best tasting properties. In this regard, we have established systems with a steady and unsteady equilibrium depending on transformation of hydroxyl protons of ethanol and water. Unsteady balance is typical for AAM used with ERS «Lux» and drinking water, with a tasting score – 9,43 points. This also include the AAM made from ERS «Lux» and demineralized water by reverse osmosis, with a tasting score – 9,30 points. The systems with a steady equilibrium are typical for AAM made of ERS «Lux» and water softened by Na- cationization, with a tasting score of 9,49 points.

Thus, in the work of Kuzmin O. et al [25-27] experimental evidence of steady/unsteady thermodynamic equilibrium of AAM were established. The established equilibriums affect organoleptic characteristics of AAM depending on water treatment method and time of system's functioning. However, the questions related to internal mechanism and speed of unsteady thermodynamic equilibrium of finished product - vodka or flavored vodka were not yet clarified.

Therefore, additional studies were required to be conducted for a more detailed study of the internal mechanism of unsteady thermodynamic equilibrium to insure provision of a high quality characteristics of finished products (vodka, flavored vodka).

The aim of this work is to identify equilibrium state of hydroxyl proton of ethanol and water in various samples of vodkas and flavored vodkas produced in Ukraine, using  $^1\text{H}$  NMR spectroscopy.

## Materials and methods

$^1\text{H}$  NMR analysis of AAM was conducted with the usage of:

- FT-NMR Bruker Avance II spectrometer (400 MHz); measurement error of the chemical shifts for  $^1\text{H} \pm 0,0005$  ppm; 5-mm broadband inverse probe with Z-gradient; thermostatic system (+25°C ... +100°C);

- Specially shaped capillary with acetone- $\text{d}_6$  ( $\text{CD}_3$ ) $_2\text{CO}$  (atomic fraction of deuterium – 99,88%; moisture content – 0,018%; bp=+56,3 °C, mp=-94 °C; chemical shift of the residual proton  $^1\text{H} \delta = 2,75$  ppm;

- High accuracy ampoules №507-HP for high resolution NMR's spectroscopy (400 MHz) standard length - 178 mm; outside diameter - 4,97±0,006 mm; internal diameter - 4,20±0,012 mm; curvature ± 0 0006 mm;

- Volumetric pipette;

- Dispenser;

- The 31 sample of vodkas, flavored vodkas and moonshine, produced in Ukraine (Table 1) were used as experimental material for  $^1\text{H}$  NMR spectroscopy.

Experimental studies of  $^1\text{H}$  NMR were carried out in the following order:

- Preparation of samples to research;
- Recording of  $^1\text{H}$  NMR spectrum;
- Conclusion and interpretation of work results.

Work methodology:

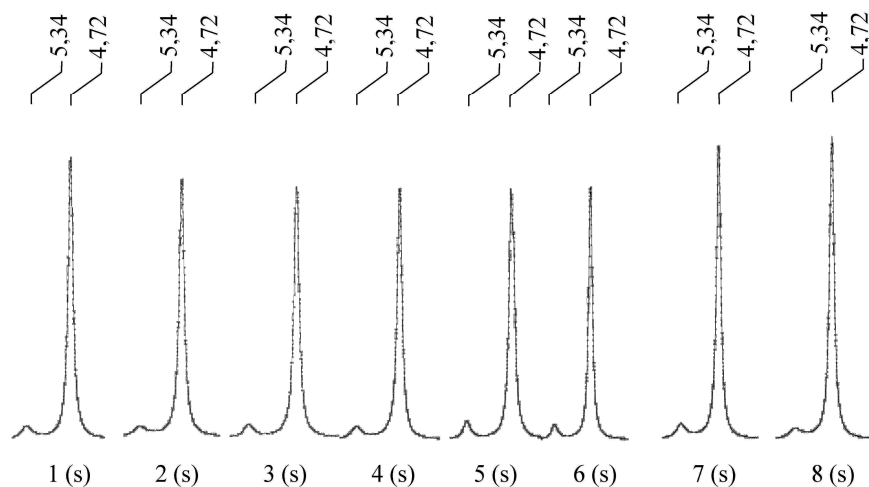
- 0,3 ml of vodka or flavored vodka prepared with a volumetric pipette with a predetermined strength ( $40,0 \pm 0,2$ )% vol. External standard separated from the testing substance which is required for LOCK's system operation (deuterium solvent (acetone- $\text{d}_6$ ) of NMR's deuterium stabilization spectrometer) is added in a special form of a capillary into an ampoule. The obvious advantage of using the external standard is the fact that standard substance's molecules and test's solution do not interact with each other;

-  $^1\text{H}$  NMR spectra records and data processing were performed according to the instruction of FT-NMR Bruker Avance II spectrometer (400 MHz).

## Results and discussions

The 31 sample of vodkas and flavored vodkas, produced in Ukraine were used as experimental material for  $^1\text{H}$  NMR spectroscopy. These samples were divided into 3 groups with unsteady equilibrium, transitional and steady equilibrium of protons hydroxyl group (Fig. 1-3).

We will study first group of vodkas and flavored vodkas with unsteady equilibrium. This group has included 8 samples of vodkas of a different manufacturers, brands, names and formulations (Fig. 1).



**Fig. 1.  $^1\text{H}$  NMR spectra of hydroxyl group protons of ethanol ( $\text{EtOH}$ ) and water ( $\text{H}_2\text{O}$ ) with unsteady equilibrium:**  
1...8 - number of the sample (Table 1)

The selected samples of vodkas and flavored vodkas with unsteady equilibrium characterized by the absence of single signal ( $\text{EtOH}+\text{H}_2\text{O}$ ), therefor hydroxyl group of protons is represented by two separate peaks of ethanol ( $\text{EtOH}$ ) and water ( $\text{H}_2\text{O}$ ).

The component of multiplet of hydroxyl protons of ethanol ( $\text{EtOH}$ ) in each sample is represented as a single broad singlet (s) with a rounded shape, located in a «weak field» with a chemical shift  $\delta_{\text{EtOH}}=5,34$  ppm.

The component of proton of water (H<sub>2</sub>O) in each sample presented as singlet (s) with a chemical shift  $\delta_{\text{H}_2\text{O}}=4,72$  ppm. Waveform of H<sub>2</sub>O protons - is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

**Table 1**

**List of samples, used as an experimental material**

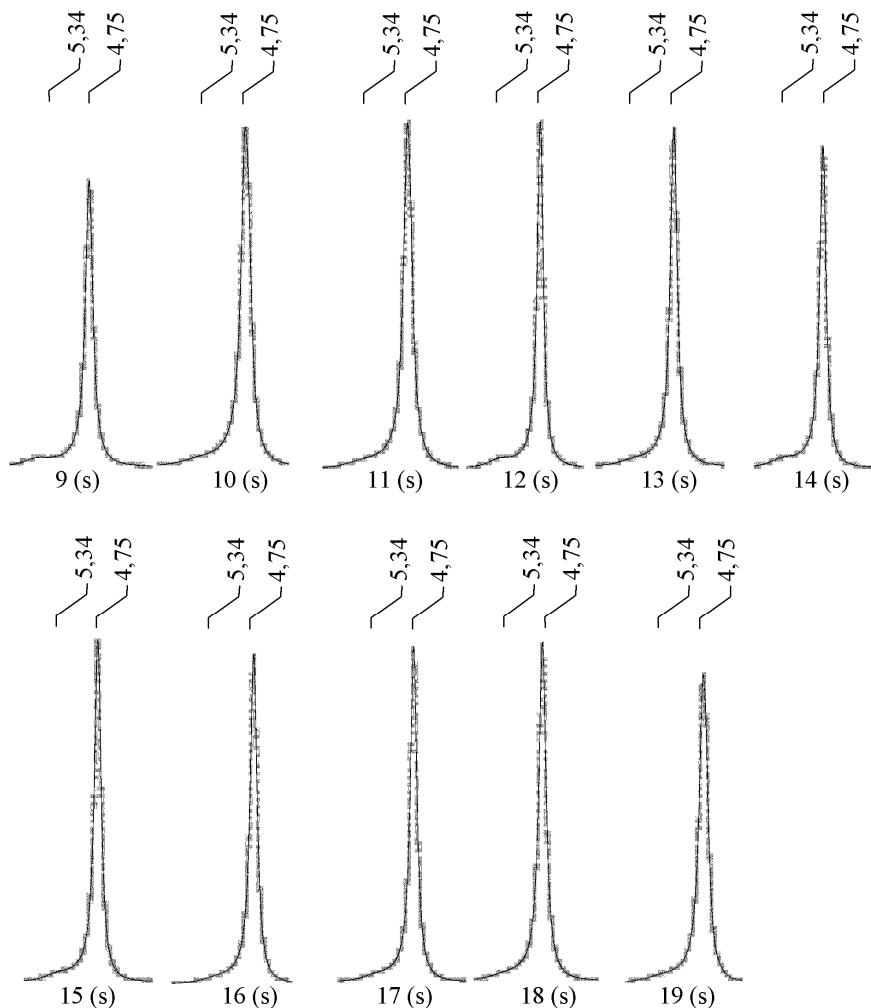
<b>№ sample</b>	<b>Name of product</b>	<b>Name of enterprise</b>
1	«Poliana Chysta» <sup>1</sup>	LLC «First Ukrainian Vodka Standard»
2	«Sprava maistra Spravzhnia» <sup>1</sup>	LLC «Distillery Altera»
3	«Medoff Classic» <sup>1</sup>	LLC «Crimean Vodka Company»
4	«Khibna sloza» <sup>2</sup>	LLC «Distillery «Karat»
5	«Istynna Sribna» <sup>1</sup>	LLC «Distillery «Prime»
6	«Vdala Zhytnia» <sup>2</sup>	CJSC «Crimean Wine and Cognac Factory «Bakhchysarai»
7	«Bilenka Pshenychna nyva» <sup>1</sup>	LLC «Distillery «Prime»
8	«Status Klasychnyi» <sup>1</sup>	LLC «Zolotonosha Distillery «Zlatogor»
9	«Nemiroff Ukrainska berezova osoblyva» <sup>2</sup>	SC «Ukrainian Vodka Company «Nemiroff»
10	«Green Day» <sup>1</sup>	LLC «Atlantis»
11	«Perepilka Klasychna» <sup>1</sup>	LLC «National Vodka Company»
12	«Zlatohor Chysta sloza M'iaka» <sup>2</sup>	LLC «Zolotonosha Distillery «Zlatogor»
13	«Khutorok Eksportna» <sup>1</sup>	LLC «Crimean Vodka Company»
14	«Nemyrivska Pshenytsia ukrainska vidbirna» <sup>2</sup>	SC «Ukrainian Vodka Company «Nemiroff»
15	«Morosha Karpatska» <sup>1</sup>	LLC RPE «Hetman»
16	«Luga-Nova Rosiiska» <sup>1</sup>	PJSC «Lugansk distillery Luga-Nova»
17	«Na berezovykh brunках» <sup>2</sup>	LLC «Crimean Vodka Company»
18	«Luga-Nova Bila koroleva» <sup>2</sup>	PJSC «Lugansk distillery Luga-Nova»
19	«Ukrainka Dzherelna» <sup>1</sup>	LLC «Atlantis»
20	«Berezovi tsvit» <sup>2</sup>	LLC «Beveridge group»
21	«Khortytsa Absolutna» <sup>1</sup>	SE «Image Holding» JSC «Image Holding AnC»
22	«Malynivka Lahidna» <sup>2</sup>	LLC «Distillery «Prime»
23	«Zoloty Lviv Panska» <sup>1</sup>	JSC «Lviv distillery»
24	«Prime World class» <sup>1</sup>	LLC «Distillery «Prime»
25	«Pulse active» <sup>1</sup>	LLC «Artemovsk Distillery-Plus»
26	«Baika Liuksova yakist Pom'iakshena» <sup>2</sup>	LLC «National Vodka Company»
27	«Nova Rublovka Klasychna» <sup>2</sup>	LLC «Latona-Invest»
28	Moonshine <sup>3</sup>	smt. Novgorodskoe
29	«Poltavska bytva» <sup>2</sup>	CJSC «Poltava Distillery»
30	«Khortytsa Platinum» <sup>1</sup>	SE «Image Holding» JSC «Image Holding AnC»
31	«Artemivska Klasychna» <sup>1</sup>	LLC «Distillery Altera»

**Note.** 1 – vodka, 2 - flavored vodka; 3 – moonshine



The difference between the chemical shifts of hydroxyl protons of ethanol (EtOH) and water (H<sub>2</sub>O) in each sample is  $\Delta\delta=0,62$  ppm. This may indicate that conditions for the formation of water structure with hydroxyl proton of alcohol were not yet set, therefore we can state that thermodynamic equilibrium didn't appear in any of the samples.

We will study second group of vodkas and flavored vodkas with transitional equilibrium. This group has included 11 samples of vodkas of a different manufacturers, brands, names and formulations (Fig. 2).



**Fig. 2.** <sup>1</sup>H NMR spectra of hydroxyl group protons of EtOH+H<sub>2</sub>O with transitional equilibrium:

9...19 - number of the sample (Table 1)

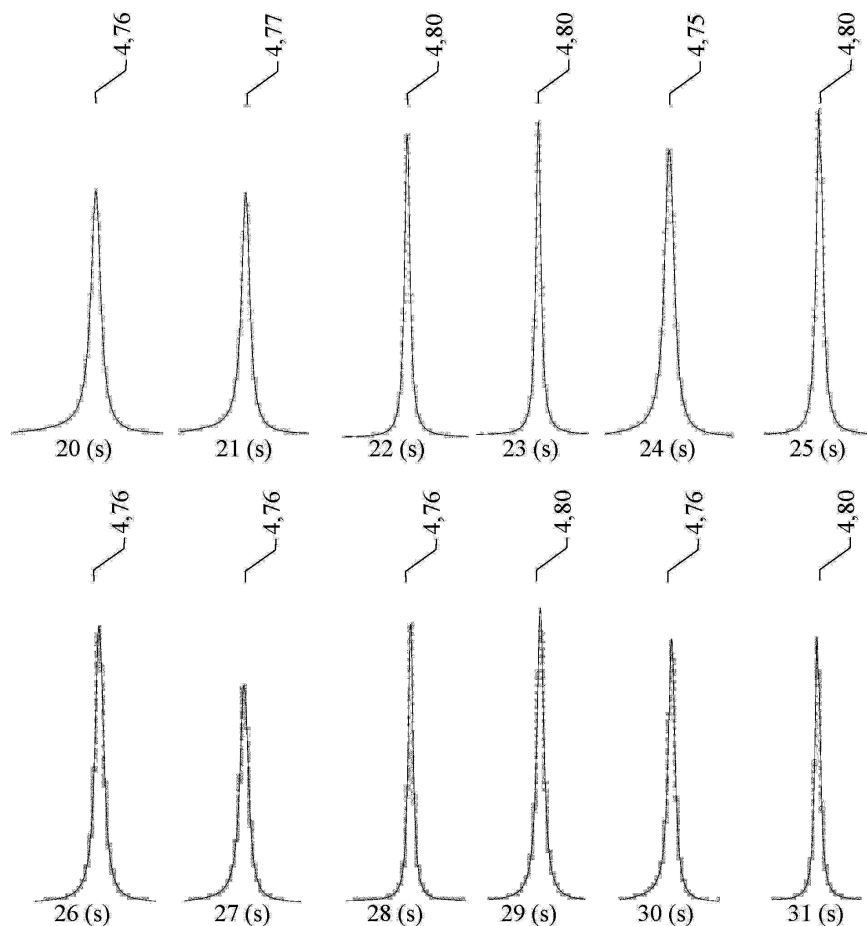
The samples of vodkas and flavored vodkas with the transitional equilibrium as well as samples with unsteady equilibrium are characterized by the absence of unitary signal (EtOH+H<sub>2</sub>O) therefore hydroxyl group of protons is presented by two separate picks of H<sub>2</sub>O and EtOH.

Component of multiplet of hydroxyl protons of ethanol (EtOH) in each sample is represented as a separate subtle signal of a rounded shape located in a «weak field» with a chemical shift  $\delta_{\text{EtOH}}=5,34$  ppm.

Component of proton of water (H<sub>2</sub>O) in each sample is represented as a singlet with a chemical shift  $\delta_{\text{H}_2\text{O}}=4,75$  ppm. Waveform of H<sub>2</sub>O signals is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

The difference between the chemical shifts of hydroxyl protons of ethanol (EtOH) and proton of water (H<sub>2</sub>O) in each sample is  $\Delta\delta=0,59$  ppm. This may indicate that certain prerequisites are created to establish equilibrium structure (unsteady/steady equilibrium).

We will consider the third group of vodkas and flavored vodkas with steady equilibrium. This group has included 12 samples of vodkas of a different manufacturers, brands, names and formulations (Fig. 3).



**Fig. 3. <sup>1</sup>H NMR spectra of hydroxyl group protons of EtOH+H<sub>2</sub>O with a steady equilibrium:**

20...31 - number of the sample (Table 1)

The selected samples of vodkas and flavored vodkas with a steady equilibrium characterized by a unitary signal of hydroxyl group (EtOH+H<sub>2</sub>O). The component of protons of EtOH+H<sub>2</sub>O in each sample presented as singlet (s), located in a «weak field» with a chemical shift, which is in a range  $\delta_{\text{EtOH+H}_2\text{O}}=4,75...4,80$  ppm. Waveform of EtOH+H<sub>2</sub>O protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

## Conclusions

We will draw conclusions on establishing of equilibrium hydroxyl proton of ethanol and water in vodka and flavored vodka by <sup>1</sup>H NMR spectroscopy. We identified three groups of samples based on the equilibrium of the hydroxyl groups of protons of ethanol (EtOH) and water(H<sub>2</sub>O): unsteady; transitional; steady.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of EtOH+H<sub>2</sub>O. Unsteady and transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of EtOH and H<sub>2</sub>O. Unsteady equilibrium is characterized by the presence of hydroxyl proton of ethanol (EtOH), which is obvious. Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium.

The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas and flavored vodkas, using <sup>1</sup>H NMR spectroscopy. Equilibrium systems allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

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## Influence ratio of water and oil phases of emulsions with starch on viscosity, density, particle size and muddy turbidity of system

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### Abstract

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**Introduction.** It is necessary to selection of optimal ratios of water and oil phases, mode selection mixing of the two phases, the selection of parameters homogenization in which a stable emulsion system.

**Materials and methods.** To study prepared 5 samples of food emulsions with a variable number of the oil phase and a constant amount of stabilizer (starch) and 5 samples of food emulsions using different amounts of starch at a constant amount of the oil phase. The viscosity of emulsion was determined at Brookfield viscometer, the particle size – at microscope Eastcolight 92012-ES (100x, 250x, 550x, 750h), the muddy turbidity – at muddy turbidity meter 2100b, the density – at laboratoru aerometer.

**Results and discussion.** Analysis of emulsion with a variable number of the oil phase and a constant amount of starch shows that the greater rate of oil phase, the higher the viscosity, turbidity, density, pH and particle size of the emulsion, but the particle size must not exceed 1 mm. Analysis of emulsion using different amounts of starch at a constant amount of the oil phase shows that the more starch in the composition of the product, the smaller the particle size of emulsion turbidity, which improves the stability of the emulsion. Increasing the number of stabilizer improves the stability of the emulsion, as the particle size decreases, but has little effect on turbidity. If insufficient quantities of stabilizer formed particles are larger than 1 micron, which may lead to a "fat ring" in the system storage. The best result of a study of emulsions with starch - is to get the maximum number of particles about 1 micron.

**Conclusions.** The results can be the basis for the technology of production of emulsions as a class of foods. Creating a stable emulsion system is a pressing issue in the food industry, so these studies are useful and important for the development of new food products.

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## Introduction

Despite the large number of studies on the use of starch in different sectors of the food industry, little attention was paid to the study of the stabilizer in food emulsions. To date, the emulsion is widely used in different sectors of the food industry. Getting a stable emulsion system is important and promising issue.

## Literature review

As the stabilizing and emulsifying ingredient in the manufacture of scented oil emulsions using starch (E 1450). Starch - is one of the most widely used thickeners and emulsifier [1].

Found that a stable, emulsions are closely associated with the mechanism of dispersion and depends on many factors, such as oil content, type and concentration of emulsifier, the route of administration phases, time and intensity and degree of dispersion and temperature. Study of factors that ensure stability of emulsion, led to the conclusion that the critical degree of dispersion [2–3].

Experiments found that for each type of emulsifier has its own optimum concentration that provides the highest resistance obtained emulsions [4]. For an introduction to emulsify oils (for each concentration of emulsifier) is also optimum in which the most stable emulsion is obtained, that are determining the optimal ratio between the aqueous and oil phases. Introduction of excess oil causing stratification. Thus for each emulsifier is its optimum concentration, the corresponding amount of oil in the emulsion [5-6].

The optimum concentrations of emulsifiers for certain ratios of the phases in obtaining stable emulsions are not fixed and depend on the degree of dispersion. The use of high-speed mixing, and especially increasing pressure homogenizer leads to increased dispersion, viscosity and the formation of more stable emulsions [7].

The process of emulsification controlled in several ways, but most commonly used viscometer Brabendera or express-methods of analysis of viscosity. Thus the dependence of viscosity starches obtained by time, temperature and shear rate. State of the starch granules can be controlled also under the microscope [8].

Starch – is one of the primary emulsifier for soft drinks, all their components are compatible with starch, including:

- citrus oils , synthetic flavors, oils when neutral vegetable oils, triglycerides, etc.;
- artificial colors, including yellow “sunset” and tartrazin and natural dyes , including carotene and maslosmoly .

The concentrated emulsion with 10–20 % fat phase in the production of non-alcoholic beverages or diluted to a concentration of 10–20 g/l in concentrated syrup with a high density of BRICS ), or to a concentration of 1–2 g/l soda water. Such stabilized emulsions can be used in obtaining flavored alcoholic beverages strength to 20 %, which starch flocculation occurs.

It is important to be able to predict the stability of the emulsion. In most cases, this is done on the basis of data on the size distribution of particles obtained by laser granulometry microscopy or emulsions at high and room temperature, and the results of observations (both visually and methods of analysis of light transmission and backscattering) per bundle emulsion and sediment. Naturally, these accelerated methods must be accompanied by long-term observation of the behavior of drinks during storage [7–8].

In emulsions such as “oil in water” starch E 1450 plays the role of an emulsifier and a stabilizer.

There are several factors that hinder the wide industrial application of native starches. One of the main factors is that native starches cannot be emulsifiers because it does not contain lipophilic balance oktenilsuktsynat, which is introduced in addition to modified starches to ensure their emulsifying properties.

Native starches have only hydrophilic residues, so as Thickeners are used in products with a short shelf life.

Modified starch emulsifier is in own way as part containing lipophilic and hydrophilic residues.

Lipophilic remains of oktenilsuktsynat provide electrostatic stability of the product, by reducing the value of the surface tension, hydrophilic residues provide mechanical stability of the product, interact with water make thicker product [9].

The process of destruction of the emulsion described rate of destabilization (V) by Stokes law:

$$V = \frac{2 \cdot r^2 (d_1 - d_2) \cdot g}{9 \cdot q}$$

where: V – speed destabilization of the emulsion;

$d_1$  and  $d_2$  – density of the dispersed phase and the dispersion, respectively;

q – the viscosity of the medium;

r – radius of the globule of fat;

g – acceleration due to gravity.

To reduce the V, you must use oil with a high density (about 1.0) or increase the density of light oil (such as citrus, which  $d \sim 0,80$ ) by making authorized for use in foodstuffs agents such as sucrose atsetatizobutirat.

To reduce the fat globules range 0.4–1.0 microns are used to mixing with a high shear stress and homogenisation of emulsions pressure 100–300 kg/cm<sup>2</sup>. With this amount of fat globule coalescence is minimized, and the dissolution is a strong turbidity.

Efficient dispersion and homogenization of the emulsion in syrup achieved with the dispersion medium viscosity 30-100 mPa s.

When homogenization pressure of 300 kg/cm<sup>2</sup> commonly used twohod and two stages system.

## Materials and method

For studies prepared 5 sample emulsions of varying oil phase and a constant number of starch ( Table 1) and 5 samples of food emulsions using different amounts of starch as stabilizer (at constant oil phase) ( Table 2)

### Preparation of emulsion with starch

**Preparation of oil phase.** Weigh the required amount of flavor; add Esther scales in stirrer at room temperature until Esther scales completely dissolved.

### Preparation of the aqueous phase (starch solution).

1. Weigh the required amount of water into a glass and heated to 20-50 ° C.
2. Attach the required amount of sodium benzoate and completely dissolve. Add citric acid and dissolve completely.
3. Attach the required amount of starch and dye solution in warm water (20-50 ° C).
4. Starch mix and dissolve at a moderate speed mixer until it is completely dissolved. Subject the immediate hydration; leave for a few minutes for aeration.

**Preparation of the pre- emulsion.** For the pre- emulsion using a high-speed mixer UltraTurrax.

Cooking pre-emulsion, slowly adding the oil phase to the aqueous phase, and then stirred at maximum speed using a high-speed blender.

**Preparation of the emulsion.**

1. Homogenized according to by following the parameters.
2. Measure turbidity, viscosity and average particle size of the emulsion.

**Parameters of the fat phase.** Temperature [° C] room temperature.

**Parameters of the aqueous phase (starch solution).**

Starch solution temperature [° C] room temperature

Mechanical mixing (Anchor mixer) (rpm) 40

**Parameters of the pre- emulsion**

Starch solution temperature [° C] room temperature

Temperature of oil phase [° C] room temperature

mechanical stirring (UltraTurrax) 20 min / 3000rpm

**Parameters of the homogenization**

Number of moves 2

Pressure is the first step / second step [bar] 200 /50

Table 1

Formulations of stable emulsion stabilizer of hydrogen and a variable number of fat phase

The ingredients of the emulsion	Content ingredient, g/kg				
	Number of emulsion				
	1	2	3	4	5
Citrus oil	40	50	55	60	70
Rezynogum (E 445)	40	50	55	60	70
Starch (E 1450)	120	120	120	120	120
Citric acid (E 330)	5	5	5	5	5
Sodium benzoate (E211)	2,5	2,5	2,5	2,5	2,5
Water	792,5	772,5	762,5	752,5	732,5
Total	1000	1000	1000	1000	1000

Table 2

Formulations emulsions with constant number of fat phase and a variable number of water stabilizer

The ingredients of the emulsion	Content ingredient, g/kg				
	Number of emulsion				
	6	7	8	9	10
Citrus oil	55	55	55	55	55
Rezynogum (E 445)	55	55	55	55	55
Starch (E 1450)	80	100	110	120	140
Citric acid (E 330)	5	5	5	5	5
Sodium benzoate (E211)	2,5	2,5	2,5	2,5	2,5
Water	802,5	782,5	772,5	762,5	742,5
Total	1000	1000	1000	1000	1000



## Results and discussion

The results of measurement of each emulsion: Brookfield viscometer - viscosity microscope EASTCOLIGHT 92012-ES (100x, 250x, 550x, 750h ) – particle size , muddy turbidity meter 2100P, lab aerometer - density, lab pH-meter - pH displayed in Table 3.

**Table 3**

**The results of measurement of the finished product**

Number of emulsion	Viscosity Brookfield, cP	Turbidity dilution 0.025 %, NTU	The average diameter of the particles of oil D, $\mu\text{m}$	Density, $\text{g}/\text{cm}^3$	pH
1	20	143	0,67	1,03	2,6
2	22	156	0,73	1,05	3,0
3	23	170	0,75	1,07	3,3
4	24	182	0,84	1,09	3,7
5	26	196	0,97	1,10	4,0
6	19	210	0,98	1,04	2,7
7	21	196	0,91	1,06	3,1
8	22	184	0,83	1,07	3,2
9	23	170	0,75	1,07	3,3
10	25	157	0,68	1,10	3,8

Analyzing the figures 1, 2, 3, 4, 5 emulsion bigger the figure the better the oil phase viscosity, turbidity, density, pH and particle size of the emulsion, but the particle size must not exceed 1 micron, and therefore the stabilizer should be enough.

Analyzing the figures 6, 7, 8, 9, 10 emulsions, characterized by an increase in the number of starch as a part of the product shows that slightly increasing viscosity, density, pH and decreasing particle size emulsion, turbidity. By continuing other components of the emulsion, the smaller the particle size, the lower the turbidity of the emulsion (but higher storage stability). If the particle size less than 1 micron, the emulsion is highly robust stability and gives some turbidity but less than 1 micron particle size, the less turbidity, if the particle size is not greater than 0.3 micron, the turbidity almost any clear solution.

For emulsion using starch as an emulsifier, selected modes and modes of stirring pre-emulsion homogenizing emulsions that provide stability during storage system.

## Conclusion

1. The best result of research in starch emulsion – is to obtain the maximum number of particles of about 1 micron.
2. If the amount of water stabilizer increased by 0.5 %, the changes of the studied parameters viscosity, turbidity and particle size of the emulsion is not significant.
3. By increasing the amount of oil phase composition of the product increases viscosity, turbidity, density, pH and particle size of the emulsion.

4. Number stabilizer may affect the stability of the emulsion, but has little effect on turbidity, with insufficient quantity of stabilizer may form a small number of particles larger than 1 micron, which can lead to the formation of «oil ring» during prolonged storage.
5. For emulsion using starch as an emulsifier, selected modes and modes of stirring pre-emulsion homogenizing emulsions that provide stability during storage system.
6. The results can be the basis for the technology of emulsions production as a class of foods. Creating a stable emulsion system is a pressing issue in the food industry, so these studies are useful and important for the development of new food products.

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## Anomalous properties in aqueous solutions of polysaccharides

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### Abstract

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**Introduction.** The study of physicochemical properties of suspensions of polysaccharides in a wide range of mechanical stress and temperature are important in justifying the technological conditions of production of quality food.

**Materials and methods.** For experiments prepared 0.5% suspension of guar gum, xanthan gum and carob gum, 1.5% suspension of pectin and 10% suspension of native potato starch in distilled water. These suspensions kept in an incubator for 30 minutes at different temperatures in the range 20-90<sup>0</sup>C.

**Results.** The existence in diffractograms studied polysaccharides broad band indicates that the dissolution of these substances in water are formed or associates polymer molecules and water. Analysis micrographs of samples polysaccharides confirm this statement. However crystallinity associates gum appears rather weak, which may be associated with features of the structure of the molecules gum with branched side chains. With increasing temperature aqueous solutions of polysaccharides above 400 C is destroyed quasicrystalline structure complex molecules, increases mobility solution, resulting in a disordered structure. This should increase the density of the solution, causing its viscosity to a temperature of 400 C, above which the viscosity begins to decrease. This anomalous behavior solutions can be explained polymorphic transformations polysaccharide molecules in the temperature range 35-55<sup>0</sup> C with increasing freedom of movement, as evidenced by the existence of exothermic peak in differential scanning calorimetry curves.

**Conclusion.** As a result of polymorphic transformations increases the activity of polysaccharide molecules in intermolecular interactions.

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## Introduction

In the newest food technologies used natural polysaccharides, which perform the functions: thickening and gelling aqueous solutions, stabilizing foams, emulsions and suspensions, slow crystallization of ice and sugar, regulate taste of food, stability of solutions during heating, transparency, control syneresis, regulation astringents properties, stability, pH and others. Easy to use polysaccharides in different manufacturing processes to create a wide range of quality food products: mayonnaises, sauces, pastes, dairy products, dairy desserts, juices, jellies, jams, salad dressings, meat products, baby foods and dietary foods, bakery products [1, 3, 6, 8, 12, 17, 18, 22, 26, 27]. Permit for the use of natural polysaccharides in the food industry has been provided by the European Commission in 1995 in the framework of Miscellaneous Additives Directive 95/2/EC.

Polysaccharides - water soluble compounds are widespread in nature. By sources of origin and their preparation can be divided into 4 groups: botanical (cellulose, starch, pectin, guar gum, carob gum, et al.), from seaweeds (agar, carrageenan, alginate), microbiological (xanthan gum, dextran, kurdlan et al.), animal (gelatin, casein, chitosan) [4, 12, 28].

Consider especially the preparation and use of certain polysaccharides that are widely used in the production of various food products.

Pectin separated from citrus and apple marc, sugar beet pulp and sunflower baskets. Important biological properties of pectin caused the presence of free carboxyl groups and hydrocarboxyl galacturonic acids. These groups are able to bind heavy metals, including radionuclides to form insoluble complexes that removed from the body.

Pectin also regulates cholesterol, improves intracellular reactions of respiration and metabolism, increases resistance to allergic factors, stimulate wound healing, speeds up the treatment of burns.

Starch - the main reserve polysaccharide of plants that accumulates in the form of granules in the cells of seeds, bulbs, tubers and in leaves and stems. Starch molecules are composed of two polysaccharides: amylose and amylopectin, and their ratio varies widely for different botanical origin of starches. As a result of physical, chemical, biological or combined effects changing the structure and properties of starch, making this polysaccharide is universal in application in the food industry.

Carob and guar gums isolated from the seeds of leguminous plants. Polysaccharide chains have a similar irregular chemical structure with alternate linear and branched zones. The use of these gums in food technology due to the following properties: the ability to form viscous aqueous solutions, synergistic interactions with other polysaccharides, leading to the formation gels of different structure, the ability to regulate the process of syneresis. These gums are not degraded in the gastrointestinal tract of humans and can be used for making baby food.

Xanthan gum is produced during fermentation by bacteria *Xanthomonas Campestris* with a molecular weight from one to several million. Xanthan is marked by three important properties that provide indispensability of this product: the ability to maintain long dispersed particles in suspension, unique pseudo ductility and resistance to intense mechanical and thermal actions. Use of xanthan gum can provide all the qualities that are necessary foods for success in today's market: stability, desired structure, presentation and natural.

According to modern research [7, 10, 19, 29, 30], polysaccharide molecules have a complex structure and exhibit the ability to form helical chains, where a special role in stabilizing this structure plays water. The behavior of colloidal polysaccharides suspensions

in food systems primarily depends on the state of water in the polymer. Branched chain polymers form different structures in space due to the existence of strong hydrogen bonds between water molecules and hydroxyl groups of polysaccharides. Such structures are not stable and may be conformational transitions under mechanical and thermal loads, which can affect the behavior of technological products processing. Therefore, the study of physicochemical properties of suspensions of polysaccharide in a wide range of mechanical stress and temperature are important in justifying the technological conditions of production of quality food.

## Materials and methods

The potato starch used in this work is commercially available and was supplied by VIMAL PPCE (Ukraine). The amylose content in the starch used was about 36% (manufacturer's data).

Apple pectin was given by ZPOW "Pektowin" S.A. (Poland), guar gum, carob gum, xanthan gum were obtained from A&Z Food Additives Co., Ltd (China).

For experiments prepared 0.5% suspension of guar gum, xanthan gum and carob gum, 1.5% suspension of pectin and 10% suspension of native potato starch in distilled water. These suspensions kept in an incubator for 30 minutes at different temperatures in the range 20 – 90°C.

Rheological behavior of prepared suspensions, heated at different temperatures, was studied on the «Reotest-2» (Germany) at room temperature.

Prepared specimens were observed using polarized light optical microscopy «Mikmed-6» (Lomo, St-Petersburg Russia).

For the X-ray studies, treated at different temperatures suspension dried at room temperature and crushed.

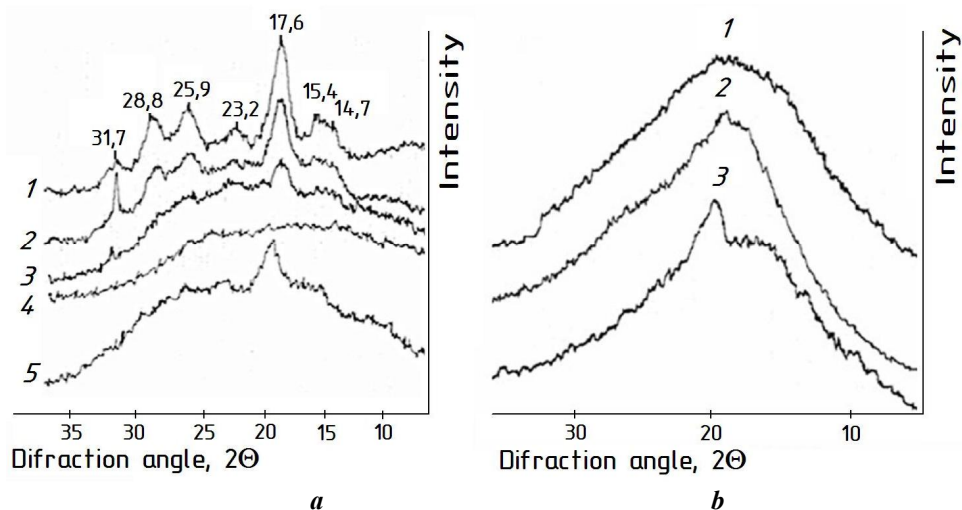
Thermal properties samples were analysed using differential scanning calorimeter DSC Q2000 (TA Instruments, USA). Samples were heated at a rate of 10°C/min from 25 to 100°C.

The X-ray diffraction analysis was performed using a diffractometer type D8 (Bruker, Germany) under the following conditions: X-ray tube, 36KV and 20mA with 0.1542 nm CuK radiation, the scan rate 4°/min, scanning from  $\theta=5^{\circ}\sim 35^{\circ}$ , step interval 0.02°, continuous scanning.

## Results and discussion

Analysis of the diffraction pattern of a number polysaccharides powders (Fig. 1 A, B) obtained in the paper and in [11, 13, 15, 25, 31, 37], indicating their identity: the background of a strong broad band in the range of 5-35° observed narrow lines that are characteristic of partially oriented crystal structures. Most clearly, they are shown for native starches, indicating a high degree of crystallinity of structural elements, which is 20 - 30% [4, 5, 21, 29, 36].

With increasing processing temperatures the crystallinity of aqueous suspensions gradually decreases and disappears completely within the temperature range 70 – 80°C. With further heating the suspension to 90 – 95°C and holding the samples at this temperature for several hours, on the diffraction pattern new narrow band, indicating retrogradation structure of the polymer [5, 14, 16, 21, 34].



**Figure 1.**

- a - X-ray diffraction patterns of native potato starch (1) and heat-treated at 60°C (2); 70°C (3); 80°C (4); 90°C (5); b  
 b - X-ray diffraction patterns of carob gum (1), pectin (2) and guar gum (3).

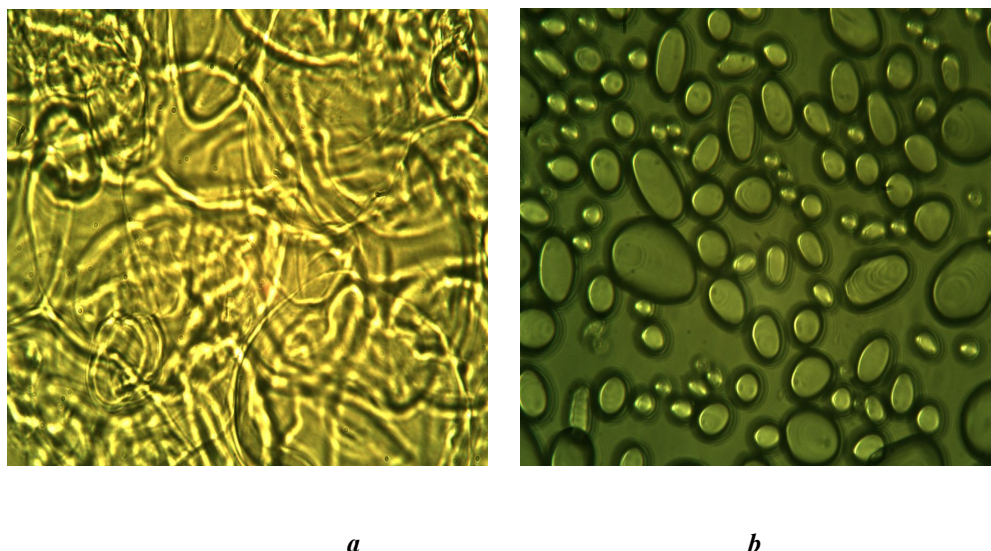
The methods of X-ray diffraction, thermal analysis and NMR spectroscopy [2, 4, 19, 33, 35, 39] shown that native starch molecules are in solution in the form of crystalline starch - water, which melted at 70 – 80°C. This greatly increases activity released from crystalline hydroxyl groups of the polymer to interact with molecules of water and other hydrophilic molecules, in particular the hydrophilic surface of dispersed minerals.

Existence of starch and various gums diffractograms broad band, indicating that when these substances dissolved in water are produced or formed associates polymer molecules and water. Analysis micrographs of samples polysaccharides that shown in Fig. 2, confirm this statement. However crystallinity associates gum appears rather weak, which may be associated with features of the structure of the molecules gum with branched side chains.

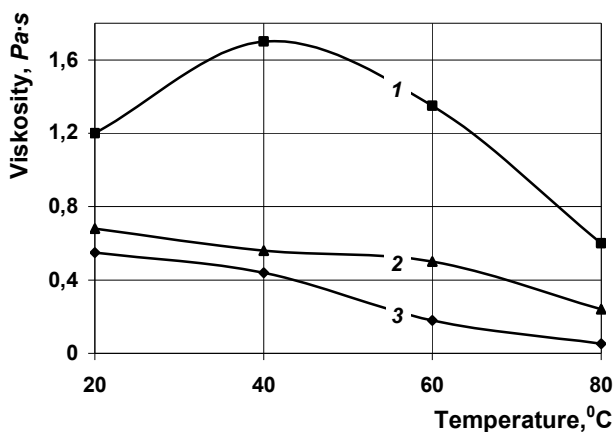
Many similar rheological behavior observed in aqueous suspensions of polysaccharides. Thus, depending on the shear strain shear all the samples are typical for non Newtonian fluids even at low concentrations of the polymer [9, 24, 32]. These dependencies can be divided into two areas: at low shear rates is the destruction of intact structure of the polymer solution, and at large - shows much lower viscosity fluid unstructured.

It is important that after the destruction of the polymer solution its structure is gradually recovering. Time to restore it more equilibrium suspensions polysaccharides, such as starch, is 18 hours, whereas for gums 1–2 hours [4]. This confirms the conclusion of a structured solution structure of starch in comparison with gums.

With increasing temperature aqueous solutions, their structure is destroyed, resulting in a decrease viscosity. However, with further increase temperature solutions gums above 40°C an increase viscosity (Fig. 3), and then it gradually decreases.



**Figure 2. Microphotograph images of potato starch suspensions:**  
*a* - native (x 400), *b* - heated to 90°C (x1000).



**Figure 3. Dependence of the shear viscosity aqueous solutions of polysaccharides:**  
 carob gum (1), xanthan gum (2), guar gum (3) on temperature.

This anomalous behavior of solutions can be explained by polymorphic transformations of the gums molecules while increasing freedom of movement, as well as anomalous behavior of water for which the temperature in the range 40 – 60°C observed optimal values physicochemical properties [38].

Conformational conversion of molecules gums also accompanied by thermal effects, as evidenced by the existence of exothermic peak in differential scanning calorimetry (Fig. 4). A similar effect was observed [29] for starch solution, whose value is 10-15 J/g. We can assume, that this exothermic effect is characteristic of all native polysaccharides.



When increasing temperature above ambient viscosity of aqueous solutions decreases. At the same time destroyed quasi-crystalline structure of the complexes molecules that are characteristic of an aqueous mixture of complexes polysaccharides in their structure.

Increased mobility of the solution molecules leads to a violation of this structure and the implementation of polymorphic transformations, giving rise to a more disordered structure. This should increase the density of the solution is increasing its viscosity to a certain temperature, above which the viscosity begins to decrease.

Thus the curve of viscosity on temperature arises optimum specific for each polysaccharide. For comparison, we can cite a famous example of abnormal changes in the density of the water with a temperature where its maximum value observed at 4<sup>0</sup>C [38]. In both cases, with increasing temperature increases the mobility of molecules, leading to the destruction of quasicrystalline structure solution and reduce its density.

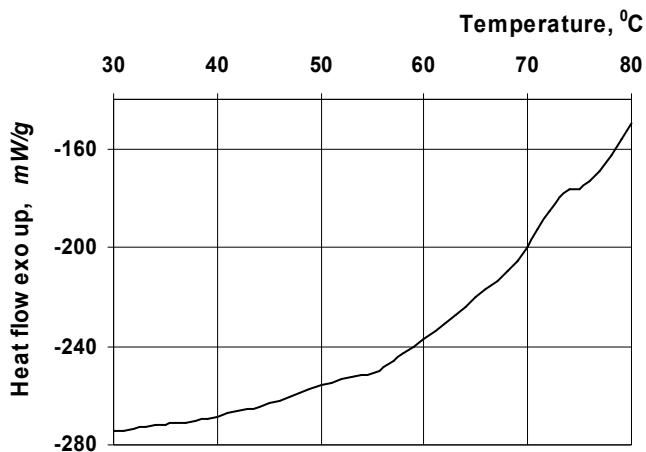


Figure 4. DSC thermograms of guar gum.

## Conclusions

The paper studied the viscosity and thermal characteristics in aqueous solutions of polysaccharides carob gum, xanthan and guar gums, pectin, starch in the temperature range 20-90<sup>0</sup>C.

Established anomalous behavior of viscosity in the temperature range 35-55<sup>0</sup>C, due to polymorphic transformation structure of biological macromolecules. This conclusion is supported by the existence of maximum thermal effect on the DSC curves.

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## Influence of partial hydrolysis on the protein extraction from sunflower meal

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### Abstract

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**Introduction.** We investigated the influence of protein hydrolysis degree in the presence of neutral protease from *Bacillus subtilis* on the process of protein extraction from sunflower meal. Correlation between protein hydrolysis degree and affectivity of protein extraction was analyzed.

**Materials and methods.** The degree of protein hydrolysis was determined as increase of TCA-soluble proteins concentration compared to control samples. Protein concentration in extracts was determined photometrically.

**Result and discussion.** Determination of protein concentration in obtained extracts have shown that main part of soluble proteins was extracted during first 20 min. The protein concentration in extracts obtained in the presence of protease was approximately twice higher than in control samples. The protein hydrolysis degree was sufficiently low and varied from 3,5 % to 5,2 % at moderate enzyme/substrate ratio. When enzyme/substrate ratio increased the degree of hydrolysis was also rising and it reached 9,0-9,5 % during 40-60 min. Such level of hydrolysis is desirable for improvement of protein functional properties and higher hydrolysis level results in loss of protein functionality. The protein hydrolysis degree was dependent from the enzyme/substrate ratio and the duration of reaction. Nonlinear model was obtained for estimation of the affectivity of protein extraction as function of enzyme/substrate ratio and extraction time. Obtained model explains 92.81% of data variation and approximates well the available data. It was shown also that high correlation ( $r=0,69$ ) exists between concentration of proteins in extracts and degree of protein hydrolysis.

**Conclusion.** The partial hydrolysis of sunflower meal proteins by neutral protease resulted in increase of protein concentration in extracts. Obtained model could be used in prediction of protein hydrolysis level during protein extraction from sunflower meal in the presence of proteolytic enzymes and their functional properties.

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## Introduction

Proteins of sunflower meal have high biological value and functional properties [1, 2]. Usually, the yield of protein isolates is not high upon extraction of proteins in water solution. Functional properties of traditional isolates need to be improved.

Partial enzymatic hydrolysis of proteins improves their functional properties and increases the field of application [3-6]. Protein hydrolysis by proteases results in synthesis of peptides with smaller molecular mass that have high solubility at high extent of hydrolysis, which is a substantially useful characteristic for many food applications. Emulsifying properties and foaming properties can be improved with limited degree of hydrolysis [7,8]. It was shown also that peptides with smaller size have better digestibility than amino acids [9].

Recently accessibility of industrial proteases from microorganisms and fungi causes the widespread hydrolysates production in the world. Most of them are from milk and soy proteins, but another source of protein, such as sunflower meal can be also used. Some authors have investigated the properties of such protein hydrolysates obtained from sunflower protein isolates [4,10].

In our previous work we have used an animal protease trypsin during protein extraction from sunflower meal [11]. We have detected the increase of protein concentration in extracts and yield of protein isolates as well as increase of solubility in wide range of pH, foam and emulsifying capacities.

In this study we have investigated the influence of protein hydrolysis degree in the presence of neutral protease from *Bacillus subtilis* on the process of protein extraction from sunflower meal. We have also analyzed the correlation between degree of protein hydrolysis and affectivity of protein extraction using.

## Materials and Methods

### *Materials*

The sunflower meal was collected from a “Melitopol oil extraction plant”, Ukraine. The protein content of meal varied from 33 to 39%. Protolad (protease from *Bacillus subtilis*, 70 units/g, Enzyme, Ukraine) was used for hydrolysis.

### *Protein extraction and obtaining of protein isolates*

Proteins were extracted from sunflower meal by sodium chloride solution (70 g/ dm<sup>3</sup>, pH 7.0) under constant stirring and temperature 40-45° C during 20-60 min, meal/solution ratio was 1:10 (w/v). Protein extraction in the presence of a protease was carried out in the same conditions at enzyme/substrate ratio from 0,25:1 to 1,75:1. In the case of enzyme applying the reaction mixture was immediately heated at 80 °C for 15 min to inactivate enzyme activity.

After this, insoluble residues were precipitated by centrifugation. The supernatant (protein extract) was used for isoelectric protein precipitation at pH 4.0-4.5. After protein coagulation, pellet was separated by centrifugation (3 000 x g), protein pellet was collected, washed and dried to 6-8 % fluidity.

### *Determination of protein concentration*

Protein contents of the extracts were determined photometrically at 540 nm according to the Biuret method [12] using bovine serum albumin for calibration. All determinations were performed in triplicate.

### *Determination of the Degree of Hydrolysis*

The degree of protein hydrolysis (DH) was determined according to Popovic et al. [13] in some modification. To a 0.5-mL aliquot of the supernatant obtained after hydrolysis, an equal volume of 0.5 mol/dm<sup>3</sup> 3-chloro-acetic acid (TCA) was added. The mixture was incubated for 30 min at 4 °C. Thereafter, the mixture was centrifuged at 7 000 rpm for 10 min. The TCA-soluble fraction and the reaction mixture were analyzed to determine the protein content by the method of Lowry et al. [14]. The DH value was calculated as the increase of TCA-soluble protein concentration in the presence of protease ( $C_{protease}$ ) to protein content in control samples ( $C_{control}$ ), expressed as a percentage:

$$DH = \frac{C_{protease} - C_{control}}{C_{control}} \times 100 .$$

*Statistical Analysis*

Data were expressed as means ± standard deviation for triplicate determinations. A least significant difference test with a confidence interval of 95 % was used to compare the means. The main results of modeling process obtained with STATISTICA program, are shown below (Fig. 1, 2, 3).

Model: Prot=exp(b0+b1*R**2+b2*T) (matr_1.sta in FoodJournal.stw)			
Dep. var: Prot Loss: (OBS-PRED)**2			
Final loss: 12,538345879 R= ,96338 Variance explained: 92,810%			
Exclude cases: 11			
N=11	b0	b1	b2
Estimate	4,024242	0,039936	0,002308

**Fig.1. Result of nonlinear estimation in STATISTICA**

Regression Summary for Dependent Variable: LN-V1 (matr_1.sta in FoodJournal.stw)						
R= ,96016152 R?= ,92191015 Adjusted R?= ,90238768						
F(2,8)=47,223 p<,00004 Std.Error of estimate: ,01965						
Exclude cases: 11						
N=11	Beta	Std.Err. of Beta	B	Std.Err. of B	t(8)	p-level
Intercept			4,029706	0,016876	238,7841	0,000000
T	0,580556	0,098833	0,002197	0,000374	5,8741	0,000372
V3**2	0,780127	0,098833	0,039188	0,004965	7,8934	0,000048

**Fig. 2. Model (2) after dependent variable transformation.**

Correlations (matr_1.sta in FoodJournal.stw)		
Marked correlations are significant at p < ,05000		
N=11 (Casewise deletion of missing data)		
Exclude cases: 11		
Variable	Prot	DH
Prot	1,00	0,69
DH	0,69	1,00

**Fig. 3. Correlation between two variables.**

## Result and Discussion

The degree of protein hydrolysis depends from the duration of reaction and enzyme/substrate ratio (Fig. 4). The protein hydrolysis degree was sufficiently low and varied from 3,5 % to 5,2 % at moderate enzyme/substrate ratio ((0,25-0,75):100). The increase of hydrolysis degree with time was statistically insufficient. As enzyme/substrate ratio increased to (1,25-1,75):100 the degree of hydrolysis was also rising and it reached 9,0-9,5 % during 40-60 min. It was shown that mainly such level of hydrolysis was desirable for improvement of protein functional properties and that higher hydrolysis level resulted in loss of protein functionality [4].

Determination of protein concentration in obtained extracts has shown that main part of soluble proteins was extracted during first 20 min (Fig. 5). The protein concentration in extracts obtained in the presence of proteases was approximately twice higher than in control samples. Only negligible part of proteins was extracted during next time of reaction at every enzyme/substrate ratio, except control samples and samples with enzyme/substrate ratio 1,75:100. The protein concentration increased by 11,6 % relatively to 20 min when reaction was carried out during 60 min at last ratio.

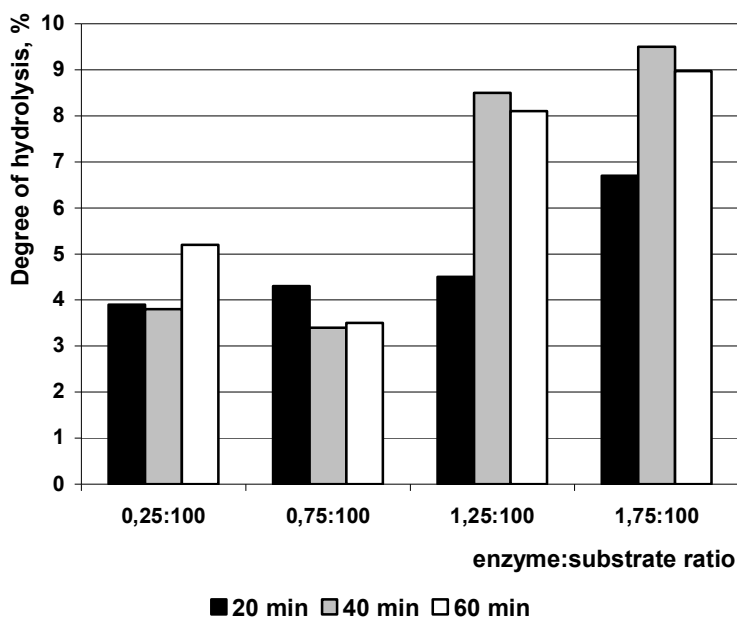
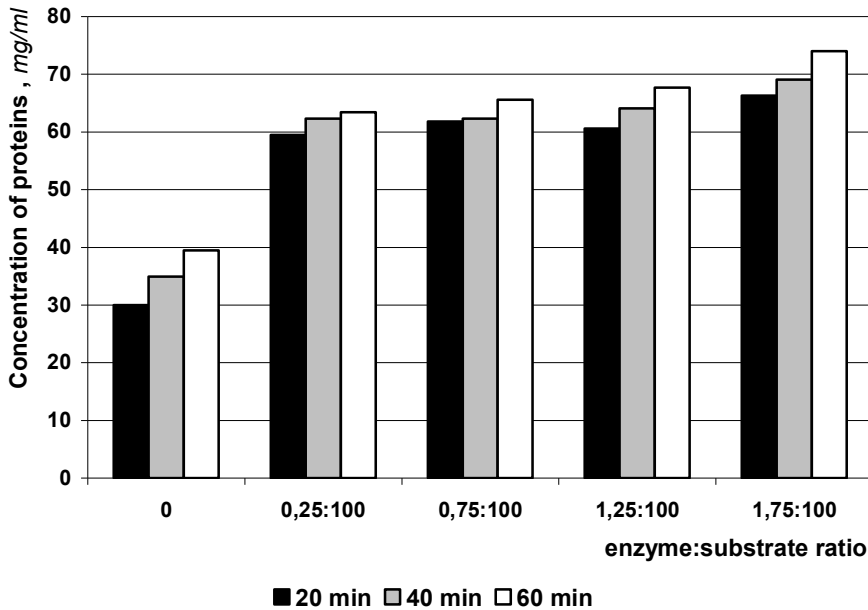


Fig. 4. The degree of protein hydrolysis dependence from the time of reaction and protease/substrate.



**Fig. 5.** Dependence the protein concentration in extracts from sunflower meal from protease/substrate and time

We have supposed that there was some relation between these two investigated parameters the degree of protein hydrolysis and protein extraction affectivity.

The experimental data for the regression model are presented in Table 1.

**Table 1**

**Experimental data for analysis in STATISTICA (v.7)**

Prot – protein concentration (random variable), mg/ml; DH – degree of hydrolysis (random variable), %; R – ratio enzyme/substrate (nonrandom variable); T – time (nonrandom variable), min.

№	Prot, protein concentration	DH, degree of hydrolysis	R, ratio enzyme/substrate	T, time
1	59,5	5,9	0,25	20
2	61,8	4,3	0,75	20
3	60,6	1,5	1,25	20
4	66,3	6,7	1,75	20
5	62,3	3,8	0,25	40
6	62,3	3,4	0,75	40
7	64,1	8,5	1,25	40
8	69,1	9,5	1,75	40
9	63,4	5,2	0,25	60
10	65,6	3,5	0,75	60
11	57,7	8,1	1,25	60
12	74,0	8,9	1,75	60



Unsatisfactory results were obtained using Multiple Regression module, but case number 11 was excluded from the analysis as outlier.

Thus, we used the Nonlinear Estimation module. Technically speaking, Nonlinear Estimation is a general fitting procedure that will estimate any kind of relationship between a dependent, and a list of independent variables. In general, all regression models can be stated as:  $y = f(x_1, x_2, \dots, x_n)$ . In most general terms, we are interested how a dependent variable is related to a list of independent variables. Generalized Linear/Nonlinear Models (GLZ) module includes efficient algorithms for fitting. We can write any type of regression equation, which STATISTICA will then fit to our data (User-Specified Regression, Least Squares and User-Specified Regression, Custom Loss).

Simplex and quasi-Newton method was used for estimation of the model parameters. Nonlinear model

$$\text{Prot} = \exp \{b_0 + b_1 R^2 + b_2 T\} \quad (1)$$

shown on Fig. 1 explains 92.81% of data variation. Conclusion: the model approximates well the available data.

Thus, we have the nonlinear model

$$\text{Prot} = \exp \{4.0242 + 0.0399 R^2 + 0.0023 T\} \quad (2)$$

We can see, that residuals of nonlinear model (2) are normally distributed (Fig. 6). The points on the graph (Fig. 7) are located along the bisector, thus the ratio of the actual data to the model predicted is close to 1.

Thus, obtained nonlinear model (2) is an estimation of the Prot variable – the affectivity of protein extraction. Fluctuations of model residuals (Fig. 8) around zero proves estimation unbiasedness.

We have a good model due to the analysis of the data, which was built on the basis of intuitive knowledge about the nature of the possible behaviour of biological data. But we still do not know whether received model evaluation coefficients are significant. Therefore, we provided more research. With corresponding transformations of the dependent and independent variables we lead our model to the linear type (3) and used our facilities to build a multi-linear regression. Obtained results are shown on Fig. 2. Estimates of the coefficients are in column B, and all of them are significant. LN-V1 is  $\ln(\text{Prot})$ ; T is Time;  $\sqrt{3} \cdot 2$  is  $R^2$ .

$$\ln(\text{Prot}) = b_0 + b_1 R^2 + b_2 T \quad (3)$$

The estimation of correlation [15] between two variables – protein concentration and degree of hydrolysis is presented on the Fig. 3. Sample correlation coefficient (Pearson's coefficient) is equal to 0.69. This indicates that high correlation exists between two functions: concentration of proteins in extracts and degree of protein hydrolysis. In addition, we found that the result is statistically significant ( $p < 0.05$ ).

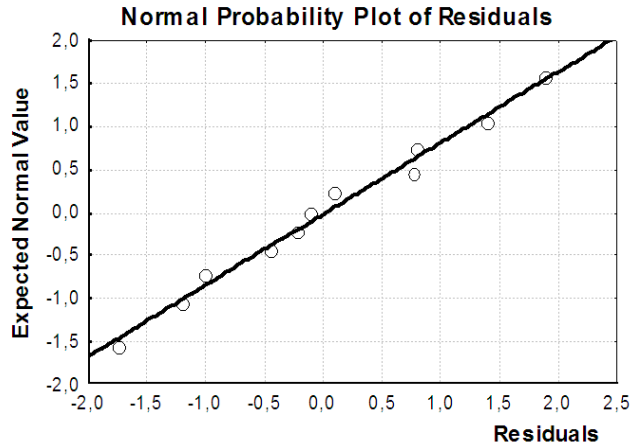


Fig.6. Residuals of nonlinear model (2)

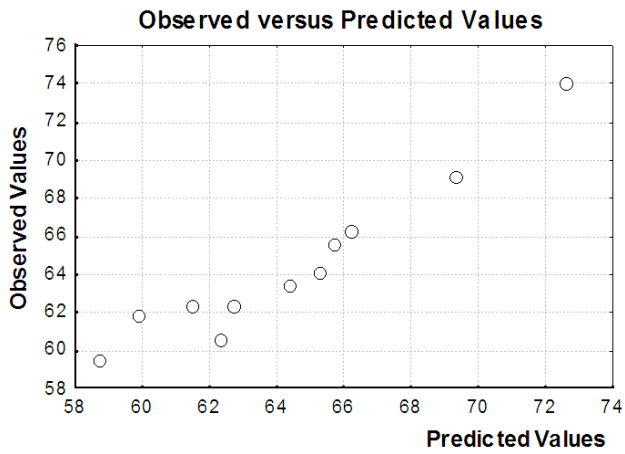


Fig. 7. Observ. vs. Predict. val. for mod. (2)

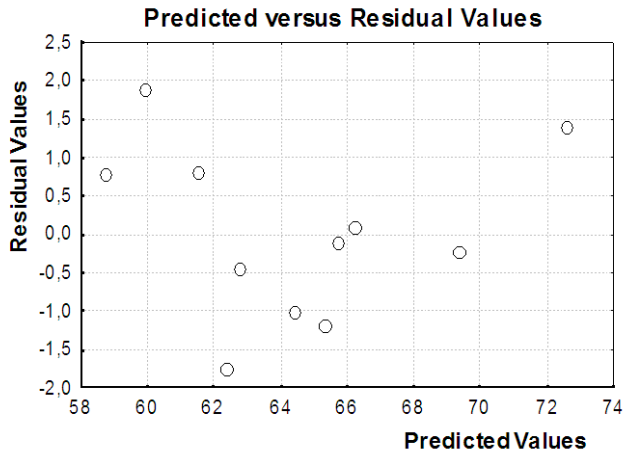


Fig. 8. Predict. vs. Resid val. for mod. (2)

## Conclusions

1. Obtained experimental results have shown that protein extraction from sunflower meal is accelerated in the presence of proteolytic enzyme as a result of partial protein hydrolysis. The degree of protein hydrolysis was not very high and depended from enzyme/substrate ratio and extraction time.
2. Nonlinear model was obtained for estimation of the affectivity of protein extraction as function of enzyme/substrate ratio and extraction time.
3. It was shown that high correlation ( $r=0,69$ ) exists between two functions concentration of protein in extracts and degree of protein hydrolysis. Linear dependence was obtained for estimation of protein hydrolysis degree using protein concentration.

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## Food products fortification by essential trace elements and human life safety: a review

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### Abstract

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**Introduction.** In humans essential trace elements (Mn, Fe, Cu, Se, Zn, I etc.) are necessary to maintain human health. Deficiency in any of these elements leads to undesirable pathological conditions that can be prevented or reserved by adequate supplementation.

**Materials and methods.** The modern literature about principles of food fortification by microelements has been analyzed. The acute toxicity, sources, relevance, essentiality, biological role and disorders, which can cause lack of these elements were reviewed.

**Results and discussion.** The supplementation should be carefully controlled given the toxic effect ascribed to trace elements when present in quantities exceeding those required for human body functionality.

It is supposed that rise of Zn consumption from 5 to 20 mg per day on human diet must be compensated for by increased up to 16 times Cu ingestion in order to maintain its balance in human body. According to experimental data, in case of one of these elements excess, both of them will become less available in human organism.

The simultaneous absorption of essential microelements in food may deep the competition between them starting from absorption in intestine to specific interaction with proteins, ligands e.t.c. The interaction between microelements may be both synergistic and antagonistic.

**Conclusions.** Most important microelements for human's health are Fe, Zn, I and Se. In our opinion bakery foods should be mainly fortified by these microelements.

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## Introduction

For a long period of time food products were thought to be a source of nutrients, necessary for the most of physiological functions including development, growth, reproductive and health. Indeed, poor nutrition, low physical activity permanent stress may cause several degenerative diseases and finally mortality rise. The recommendations of the most competent dietitians have been come to the food fortification by dietary fibres, polyunsaturated fatty acids, antioxidants, additives etc. Last decades, the attention of nutritionalists was focused on microelements deficiency impact on the development of some chronic diseases.

It is known that 23 chemical elements have physiological activity in human body, 11 from them consisted in negligible quantities and they are called essential microelements. Most of them are within 4 period (V, Cr, Mn, Fe, Co, Cu, Zn, Se), F placed in the second period, whereas Mo and I – in the sixth. Requirements for these microelements are less than 50 mg per day, while for the I, Se and F the average daily intake is sufficiently lower. The human body contains biometals, such as Fe, Cu, Zn, Mn, Mo in negligible quantities, whereas nonmetals, such as I, F and Se are found in trace amounts. Nevertheless, they are essential for the normal activity of living organisms.

Biometals being incorporated into the proteins give rise to the metalloproteins formation. These intermediates would further react with small molecules, such as phosphates, phenols, phytates resulting in the accumulation of complexes being important in human health. The biometals contained in ferments, vitamins, hormones actively participated in myriads of metabolism mechanisms, regulate activity of some body functions, and have anti-inflammatory, antiallergy and tourniquet properties.

Metals with unpaired electrons assigned to the radicals and their corresponding ions are the ion-radicals. They are able to catalyze free radical reactions, the peroxides in their presence are almost fully decomposed. Several cations, such as  $\text{Fe}^{3+}$ , often having both anti- and prooxidant properties, depending on concentration and reaction conditions. Selenium usually is an antioxidant. Cation  $\text{Zn}^{2+}$  with fully completed electronic configuration  $3d^{10}$  often being acted as an antioxidant, which substituted other prooxidant metals.

The microelements in human body can be described as the nanostructures, affected on its physiological, toxicological and biological properties. Deficiency or excessive intake of the certain trace elements resulted in the occurrence of the different acute and chronic diseases. The strategy of food fortification, based on the thesis “the more the better” was failed.

## Materials and methods

The modern literature about principles of food fortification by microelements has been analyzed. The acute toxicity, sources, relevance, essentiality, biological role and disorders, which can cause lack of these elements were reviewed.

## Result and discussion

Indeed, essential microelements deficiency is a factor that promotes the physiological changes in living organisms and demands suitable food fortification by trace elements. Furthermore, an uncontrolled intake of these compounds may cause toxicological effect on human body. For instance, Mn adequate daily intakes for man and woman are 2,3 and 1,8 mg, respectively, whereas the upper level of manganese daily consumption is 11 mg. An

excessive Mn intake being especially dangerous for brain leads to Parkinson disease. The recommended iron intakes for man and woman are 8 and 18 mg per day, respectively at the upper level 45 mg per day. In the event of chronic iron intoxication, its may be a reason of genetic and metabolic diseases. The recommended daily intake of Cu is 0,9 mg, while the upper limit is 10 mg per day. An acute copper intoxication resulted in several gastrointestinal disorders. An adequate amount of Zn is 11 and 8 g per day for man and woman at the upper limit 40 mg per day. Increased intake of zinc (approximately 150-450 mg/day) is linked to reduced Cu intake, high density lipoproteides level, has changed Fe functioning and affected on immune function. The recommended Se daily intake is 55 µg and the maximum 400 µg. Over exposure (more than 1 mg/l) may leads to several diseases, including gastrointestinal, hair and nail lost, irritability e.t.c. Thus, the fortification of foodstuff by essential microelements must be thoroughly regulated taking to account that the margin between adequate and toxic intake of the most of them is a quite narrow.

Questions about metabolism differences and interactions of the certain microelements at their cooperative presence in the human body, deficiency or excess are the key in the science of human health and intensively being studied last years. Current WHO (World Health Organization) opinion holds that main target of the healthy nutrition supply of the population of the World is an overcoming of hypoelementosis, caused by micronutrients malnutrition, which resulted in the microelements disbalance and finally in metabolism disorders and chronic diseases. At the same time, excessive intake of the most of trace elements, especially with toxic effect, such as Hg, Pb, Cd, Zn, Cu may lead to severe disease called toxicosis.

Factors that affects essential microelements digestibility are the form of chemical compound, its concentration in food, absorption mechanisms, competition for specific transport channels, quantity of proteins, especially those of animal origin, carbohydrates e.t.c. The more amount of dietary fibers, phosphates, phytates, oxalates and complex forming agents in the food, the stronger depressed microelements desorption in the gastrointestinal tract.

The simultaneous absorption of essential microelements in food may deep the competition between them starting from absorption in intestine to specific interaction with proteins, ligands e.t.c. The interaction between microelements may be both synergistic and antagonistic. Certain essential microelements have negative impact on the activity of others, while some of them can increase it. Excessive intake (hyperelementosis) of cadmium and lead have been observed in the industrial regions of Ukraine, whereas lack amount of some essential elements including Fe, Zn, Cu, Se, I. The most acute problem, which has been observed in Ukrainian urbanized regions is a toxic action of cadmium called cadmiosis. This element hardly removed from the human body, where it accumulated, primarily in liver and kidneys even at low concentrations.

According to WHO recommendations the allowable daily intake of cadmium is no more than 0,3-0,4 mg. Low concentrations of Ca, Fe as well as proteins resulted in the rise of Cd absorption. At the same time, Co, Se, Zn and its compounds can reduce the cadmium toxicity. It should be noted, that toxicity of cadmium, even at low its content in food, may be increased in case of deficiency of mineral compounds. Generally, the activity of various ferments is inhibited by cadmium due to interlocking and binding of SH groups of low molecular weight metal containing complexes. The metallothioneins containing too much SH-groups, which are able to bind both cadmium and zinc. The ionic radius of these metals is almost equal, 0,083 and 0,099 nm respectively. Thus, metallothioneins t can bind both of them. Interactions of these metals is antagonistic, zinc is replaced from most of biological systems at the excessive intake of cadmium [2].

Zinc is essential microelement for human organism, which participated in synthesis of several ferments [5]. It is well known, that zinc functions included growth, reproductive, vision, immune defense, molecular recognition, insulin and collagen synthesis, bones mineralization, neurogenesis, neurotransduction, formation and development of genitals e.t.c. Zinc is necessary for DNA synthesis, cell growth and division, proteins synthesis and functionality of many tissues and systems of human organism [5].

The question about chemical form of microelement is still controversial. Fortification of food products by microelements in the form of inorganic compounds is seems to be undesirable due to its low biological availability. Furthermore, there is a small range between adequate intake and toxic action of this microelement. The fortification of food by organic nanosalts is supposed to be more promising. But the toxic action of these compounds is still unknown.

Abnormality of zinc metabolism related to several diseases, such as leucemia, atherosclerosis, endemic goiter and others. High level of zinc in human body can cause cancer. According to the medical recommendations, daily zinc intake must be no more than 15 mg. Digestion of the recommended quantity of Zn favoring cadmium replacement in metalloproteins and retards development of virus diseases. In 2000 International zinc Nutrition Consultative group was established in order to control its deficiency in corresponding groups of risk as well as UNICEF and International Atomic Energy Agency (IAEA). A problem of zinc interactions with other essential microelements is still unresolved [5]. Thus, according to the medical assays, combinations of Zn and Fe resulted in the drop of status both of these elements, which can be explained by the competitive interactions at the time of food ingestion. Therefore, it is necessary to determine optimal dosage of Fe and Zn in order to eliminate their simultaneous deficiency.

Interaction between Zn and Se is synergistic, according to literature data, both of these microelements are incorporated into ferments in the processes of antioxidant defense. Se, Cu and Zn, being a component of ferments protect human body from free radicals. Superoxide radicals are reduced give rise to the hydroperoxides, in the presence of superoxidodismutase and Zn and as cofactors. Further, these peroxides are interacted with selenium containing glutathionperoxidase with molecules of water accumulation.

The Cu-Zn interactions have not been studied well, the obtained data are controversial. But, low proteins intake and high level of Zn may cause Cu deficiency. It is supposed that rise of Zn from 5 to 20 mg per day on human diet must be compensated for by increased up to 16 times Cu ingestion in order to maintain its balance in human body. According to experimental data, in case of one of these elements excess, both of them will become less available in human organism. Thus, rise of Fe daily intake by 10-15 times more than the physiological quantity resulted in the inhibition of absorption of the other microelements, particularly Cu, Mn and Co.

## Conclusions

In conclusion, the microelements in human body are in the equilibrium and their availability is a higher at the quantity equal to human demand. In this case the microelements are almost fully utilized in the biochemical processes and competition between them is negligible. Many countries have requirements considering the restrictions of food fortification by essential microelements and Japan, Great Britain and USA among them [11-15].

The detailed studying of the microelements interactions in human body allow to resolve the problem of diseases treatment and prevention, which caused by microelements



imbalance and will support to the effective and safe protectors of all human organs searching . The new microelements composites development and their utilization in the human diet correction are necessary to resolve the above mentioned problems.

It has been found that the most important microelements for human`s health are Fe, Zn, I and Se. In our opinion bakery foods should be mainly fortified by these microelements.

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## Effect of bee products on the structural, mechanical and physico-chemical properties of yogurt

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### Abstract

**Introduction.** Is proposed to increase yogurt's biological and probiotic value by addition of bee products. Is determined by their effect on consumer properties.

**Materials and Methods.** The raw materials used normalized milk starters of sublimation drying acacia honey royal jelly, bee pollen. The rheological parameters were determined using rotational viscometers. The degree of syneresis was determined by filtering Water-retaining capacity by centrifugation. To determine the relative viscosity using viscometer expiration.

**Results and discussion.** The study of effective viscosity of the samples showed that the addition of honey to yogurt in an amount 5% increases the effective viscosity during a slight fracture of the bunch at  $28 \pm 1\%$  and decreases during the high fracture at  $72,5 \pm 2,5\%$ . Samples with honey and royal jelly had destroyed the fastest and had the highest degree of fluidity – 0,451, but their thixotropic ability was higher than in controls. Adding honey to yogurt, royal jelly and pollen in combination helps to stabilize the viscosity and accelerate recovery after the destruction of its structure. This will help improve the consistency after pouring by the reservoir way of production. The least resistance to moisture exchange had samples with a mixture of honey and royal jelly – 42 ml WRC = 52%. The highest – with 5% of honey – 39 ml, WRC – 55%, respectively. The sample containing honey, royal jelly and pollen had a not the highest properties syneresis of the studied samples yogurt – 40ml WRC – 54,5%, but all parameters exceeded the control. Titrated acidity of the yogurt samples with five percent of honey grew faster during 9 days compared with the control and other samples. On the sixth day of storage, it was more than  $150^\circ \text{T}$ . This is above the allowed level for  $10^\circ \text{T}$ .

**Conclusions.** The best performance had a prototype, which was composed of honey, royal jelly, pollen in number – 5; 0,2 and 0,15%, respectively.

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## Introduction

The primary structure of yogurt, its preservation and restore during the production and during the warranty period depends on the processes of the bunch and acid coagulation of casein. Formation of a clot is done by converting the colloidal system of milk free-dispersed state (sol) in conjugate-dispersed (gel). Small amount of thixotropic-negotiable bonds is typical for yoghurt.

Structural and mechanical (rheological) properties, water-retaining capacity and synergetic properties of yogurt depend on the composition of milk, modes of thermal and mechanical treatment and in many ways - on the dose and type of biological agents that provide the milk fermentation. Stimulate their development in yogurt can using natural bee products [1-3].

Fillings and dose of their application affects yoghurt consistency. The extent and nature of this influence is investigated sensory and using more objective – instrumental and analytical methods.

Russian scientists have conducted research in this area and found, among other things, the positive effects of honey (honey mass fraction in the final product – 10%) on the organoleptic properties of the product prototypes [4].

Krasnikova L.V. and others. (2011) studied the rheological properties of the functional whey dessert with honey adding and found that the organoleptic and structural and mechanical properties of a dessert improved [5].

The data with the results of study of the effect of royal jelly on rheological, synergetic properties and acidity in fresh yogurt and during its storage have not been found either in Russian or Ukrainian sources.

The aim of the research was to determine the effect of bee products for texture and acidity of the yogurt.

Objects served:

- prototypes yogurt obtained in the laboratory using natural biologically dresser – honey, royal jelly and bee pollen from cow's milk with a mass fraction of fat – 3,2%;
- control samples obtained in similar conditions without adding any extenders.

## Materials and Methods

The present study was performed at the National University of Life and Environmental Sciences of Ukraine, Kiev.

The raw materials used to produce yogurt were: normalized milk base, starters of sublimation drying series of DVS-culture, acacia honey, frozen royal jelly, bee pollen crushed to a particle size of 5-10 microns.

The fat content regulated to the desired level in a milk, homogenized using pressures of 15 MPa, and at a temperature range between 55 and 65° C. Milk was inoculated with 2.5% of commercial yogurt culture (containing *Str. Thermophilus*, *Lbm. Acidophilum* and *Lbm.bulgarium* in the ratio 1:1:1) at 30-40° C °C. Samples were incubated until pH 4.6 was reached. Samples were immediately cooled to 4°C and held at that temperature during 14 days.

The fat content regulated to the desired level in a milk , homogenized using pressures of 15 MPa, and at a temperature range between 55 and 65°C. Then Milk was heated 87±2° C for 12±3min.

To determine the relative viscosity using viscometer expiration.

Measurements of viscosity were done with rotational viscometer, as formerly described by Denin Djurdjević et al., 2001 [6]. Cylindrical measuring system S1 were used with cylinder diameter ratio of 0,94.

Strain rate varied from 0 to  $140\text{s}^{-1}$ . Counting was performed in 10 min. after turning on the appropriate speed at  $8\text{-}10^\circ\text{C}$ .

The degree of syneresis was determined by filtering 100 ml of sample yogurt (on the sixth day of storage) through a filter paper for 3 h with a temperature of  $10\pm 2^\circ\text{C}$ .

Water-retaining capacity (WRC) by centrifugation at separation factor  $F = 1000$  [7]. A sample of yogurt ( $10\text{ cm}^3$ ) was centrifuged for 60 minutes with 15 min. step and measured the volume of centrifugate in ml.

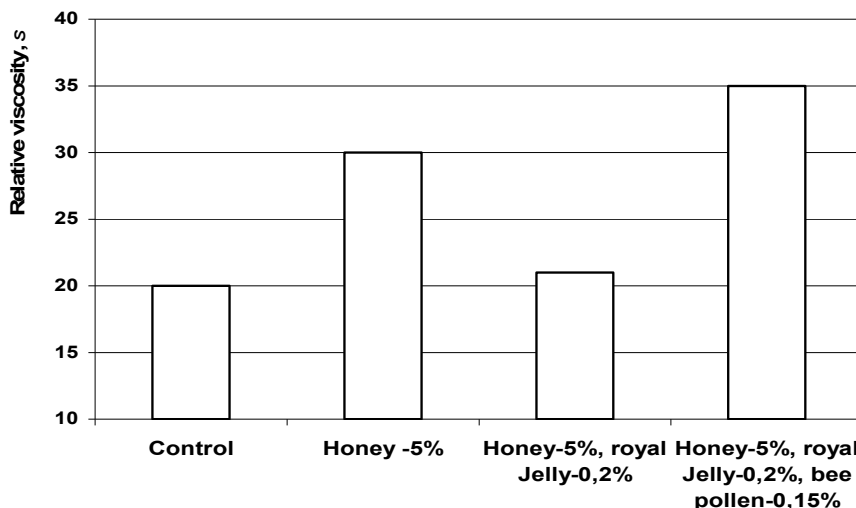
Active acidity measured by pH-meter Checker. All samples started until they reached the acidity of 102,5 T and  $\text{pH} = 4,5$  (fresh). Cooled to  $10\pm 2^\circ\text{C}$  and traced the growth dynamics of acidity on the third, sixth and ninth days of storage in the refrigerator in a sealed package.

All studies were performed three times repeatability. Statistical analysis of the experimental data was performed using Excel, confidence level of  $P \leq 0,05$ .

## Result and discussion

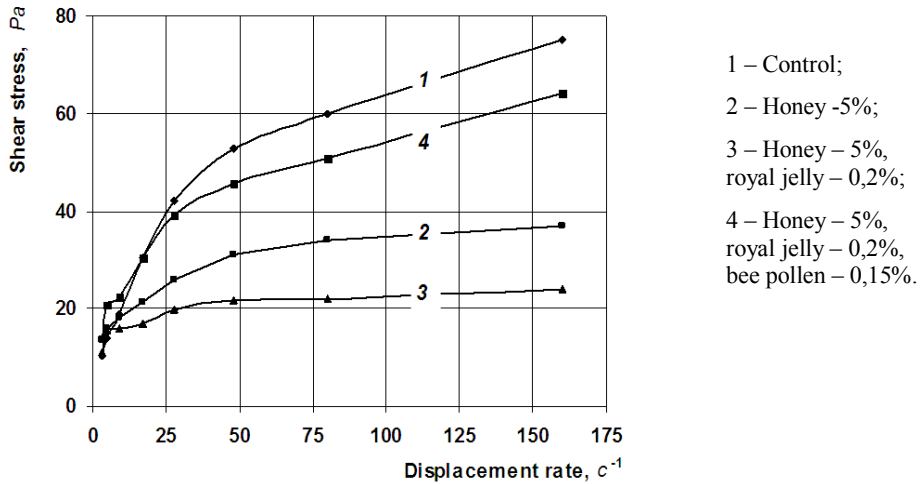
Results of the study of effective viscosity of the samples showed that the addition of honey to yogurt increases the effective viscosity during a slight fracture of the bunch at  $28 \pm 1\%$  and decreases during the high fracture at  $72,5 \pm 2,5\%$ .

Samples with honey and royal jelly had destroyed the fastest and had the highest degree of fluidity – 0,451, but their thixotropic ability was higher than in controls. Adding honey to yogurt, royal jelly and pollen in combination helps to stabilize the viscosity and accelerate recovery after the destruction of its structure. This will help improve the consistency after pouring by the reservoir way of production. As a result of relative viscosity (Fig. 1) becomes clear that the investigated samples can be attributed to pseudo-plastic fluids [6].



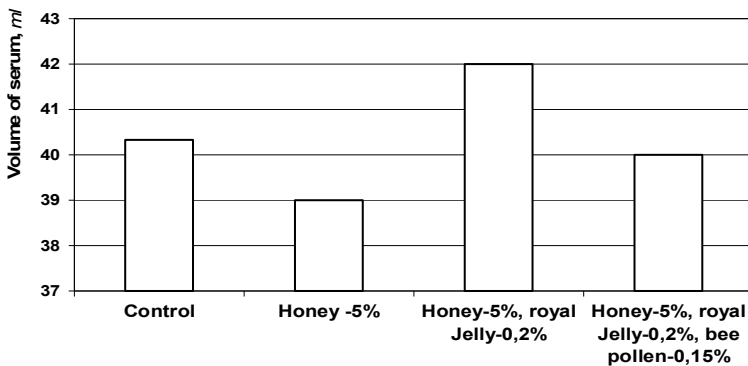
**Fig. 1. Relative viscosity of different yogurts**

All samples had the same character flow (Fig. 2). However, for the structure destruction of investigated samples it requires less efforts at  $40,7 \pm 26\%$  than for the controls. This is positive for technological process of yoghurt manufacture with bee products by reservoir method.



**Fig. 2. Shear stress of yogurt samples**

The research capacity of dairy clusters to give moisture independently and under the influence of centrifugal force (Fig. 3) showed that the least resistance to moisture exchange had samples with a mixture of 5% of honey and 0,2% of royal jelly– syneresis = 42 ml, WRC = 52%. The highest – with 5% of honey – 39 ml, 55%, accordingly. The sample containing 5% of honey, 0,2% of royal jelly and 0,2% of pollen had a not the highest properties syneresis of the studied samples yogurt, but all parameters exceeded the control.



**Fig. 3. Synergistic properties of yogurt samples**

Bee products affect the growth rate of the acidity of yogurt (table). Titrated acidity of the yogurt samples with five percent of honey grew faster during 9 days compared with the control and other samples. On the sixth day of storage, it was more than 150° T. This is above the allowed level for 10° T.

### Growth acidity of yogurt with different content of fillers

Treatments	Storage periods (days)			
	Fresh	3	6	9
Titrated acidity, °T				
Control	102,5	115,0	129,0	147,5
Honey – 5%	102,5	131,5	150,4	196,3
Honey – 5%, royal Jelly – 0,2%	102,5	117,8	137,0	160,9
Honey – 5%, royal Jelly – 0,2%, bee pollen – 0,15%	102,5	117,8	125,3	139,3
Active acidity, pH				
Control	4,50	4,37	4,20	3,93
Honey – 5%	4,50	4,28	4,00	3,30
Honey – 5%, royal Jelly – 0,2%	4,50	4,35	4,04	3,37
Honey – 5%, royal Jelly – 0,2%, bee pollen – 0,15%	4,50	4,32	4,21	4,03

The combination of honey, royal jelly and pollen stabilized the acidity of investigated yogurt specimen and for nine days held it within the framework of acceptable level [8]. Perhaps this is due to antibacterial properties of royal jelly and bee pollen stimulating properties.

Yogurt made with the addition of some bee products and their combinations, acquired new physical and chemical properties and properties of consistency. The best performance had a sample, which was composed of honey, royal jelly, pollen in number – 5; 0,2 and 0,15%, respectively. He is best restored after the destruction of the structure of the bunch, had the desired viscosity, well maintained in the structure of the bunch moisture. The acidity of the yogurt that contains: natural bee products, initially tends to accelerate growth, compared to the control sample acidity. This is probably due to stimulating properties of fillers made with respect to the dairy process.

## Conclusions

Treatment of normalized bovine milk bee products, may be, a promising direction to improve of yogurt. Honey, royal jelly and bee pollen showed significant effect on rheological and sensory characteristics of yogurts.

From the foregoing results it could be concluded that, yoghurt can be successfully made using 5% bee honey, 0.2% royal jelly, 0.2% bee pollen. The final product is best restored after the destruction of the structure of the bunch, had the desired viscosity, well maintained in the structure of the bunch moisture.

The acidity of the yogurt with natural bee products has a tendency to accelerate growth, compared to the control sample acidity.

This is probably due to stimulating properties of fillers made with respect to the dairy process. The data obtained will form the basis biotechnology of yogurt with bee products.

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## Fast Fourier transform algorithms in the spectral signal processing in real-time systems

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### Abstract

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**Introduction.** Algorithms for implementing Fast Fourier Transforming (FFT) in the digital signal filtering systems that reduce amount of computation and processing time "sliding" ("running" or "galloping") a sequence of discrete oscillations. **Materials and methods.** Using a single matrix approach to the algorithm of fast discrete Fourier transforming.

**Results and discussion.** The discrete Fourier transforming of finite sequence of samples is represented in a complex matrix form, that allows to define the structure of full parallelization process of spectral processing on the basis of principle of thinning time or thinning frequency for the "sliding" a sequence of discrete oscillations. Using a single matrix approach to the FFT algorithm, algorithms to implement operation "sliding" spectral analysis with maximum use of spectral information for the previous position "time window" are developed. Moreover, when the matrix approach is used, algorithm contains the main grouping fragments to efficiently parallelize the computational process on the basis of principle of thinning time or thinning frequency, including for the "sliding" a sequence of discrete oscillations.

For example, the values of "turning multipliers" are designed for the discrete Fourier transforming of a sequence of 16 samples of radar signal with "step-slip"  $\Delta n=4$ . For 16 samples for the next "time window" 12 (3x4) of the 16 (4x4) values at the output of the processing module is not recalculated (the rows 2-4 of 4 elements of the first "window" are the rows 1-3 of the second "window", the rows 2-4 of the second "window" are the rows 1-3 of the third "window", etc.), and only 4 of 16 must be calculated at each step of "slip".

**Conclusions.** The proposed algorithms significantly reduce the amount of computation and can be used, for example, in automated systems for digital spectral analysis of radar signals operating in real time.

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## Introduction

To solve the problems of spectral analysis, in digital signal processing devices it can be used the principle of the “sliding” (“running” or “galloping”) window. This principle is implemented on the basis of the discrete Fourier transform (DFT) or the discrete Hartley transform (DHT). To reduce the time of these transforms, it is used a variety of algorithms of the fast transforms, namely, the algorithms of the fast Fourier transforms (FFT) and the algorithms of the fast Hartley transforms (FHT).

## Materials and methods

The discrete Fourier transforming of finite sequence of samples is represented in a complex matrix form, that allows to define the structure of full parallelization process of spectral processing on the basis of principle of thinning time or thinning frequency for the “sliding” a sequence of discrete oscillations.

## Result and discussion

The DFT of a finite sequence  $\{x(n)\}$ ,  $0 \leq n \leq N-1$ , is defined by the formula [1]

$$X(k) = \sum_{n=0}^{N-1} x(n) \cdot e^{-j \cdot 2\pi n k / N} = \sum_{n=0}^{N-1} x(n) \cdot W^{nk} \quad (1)$$

where  $W = e^{-j \cdot 2\pi / N}$ ,  $k = 0, 1, 2, \dots, (N-1)$ . In formula (1) the sequence  $W^{nk}$  is a periodic sequence with the period  $N$ , i.e.  $W^{(n+mN)(k+lN)} = W^{nk}$ ,  $W_N^2 = W_{N/2}$ ,  $W_N^{k+N/2} = -W_N^k$ ,  $m, l = 0, \pm 1, \dots$ . The DFT  $X(k)$  can be read as follows

$$X(k) = \begin{cases} X_1(k) + W_N^k \cdot X_2(k), & 0 \leq k \leq \frac{N}{2} - 1 \\ X_1\left(k - \frac{N}{2}\right) - W_N^{k - \frac{N}{2}} \cdot X_2\left(k - \frac{N}{2}\right), & 0 \leq k \leq \frac{N}{2} - 1 \end{cases} \quad (2)$$

where  $X_1(k)$  and  $X_2(k)$  are the  $N/2$ -point DFT of the sequence of even elements  $x_1(n) = x(2n)$  and the  $N/2$ -point DFT of the sequence of odd elements  $x_2(n) = x(2n+1)$ , respectively.

The process of calculation of the FFT with the decomposition of the processed signal sequence into the even and odd parts (2) is called the decimation-in-time.

If it is used an another way, namely, the decimation-in-frequency than the input sequence is decomposed into the two sequential parts

$$X(k) = \sum_{n=0}^{N/2-1} x(n) \cdot W_N^{nk} + \sum_{n=N/2}^{N-1} x(n) \cdot W_N^{nk} = \sum_{n=0}^{N/2-1} x(n) \cdot W_N^{nk} + \sum_{n=N/2}^{N-1} x\left(n + \frac{N}{2}\right) \cdot W_N^{\left(\frac{n+N}{2}\right)k} = \\ = \sum_{n=0}^{N/2-1} [x_1(n) + e^{-j\pi k} \cdot x_2(n)] \cdot W_N^{nk} \quad (3)$$

The even and odd samples of the DFT of the input sequence  $X(2k)$  and  $X(2k+1)$  are the  $N/2$ -point DFTs of the sequences  $f(n)$  and  $g(n)$

$f(n) = x_1(n) + x_2(n)$ ,  $g(n) = [x_1(n) + x_2(n)] \cdot W_N^n$ ,  $n = 0, 1, \dots, (N/2 - 1)$ , which can be read by the formulae

$$\begin{aligned} X(2k) &= \sum_{n=0}^{N/2-1} [x_1(n) - x_2(n)] \cdot W_N^{2nk} = \sum_{n=0}^{N/2-1} f(n) \cdot W_{N/2}^{nk}, \\ X(2k+1) &= \sum_{n=0}^{N/2-1} [x_1(n) - x_2(n)] \cdot W_N^{n(2k+1)} = \sum_{n=0}^{N/2-1} g(n) \cdot W_{N/2}^{nk}. \end{aligned} \quad (4)$$

If a sequence of  $N$  samples of the input signal is rows arranged in a matrix of dimension  $[L \times M]$ , where  $L$  and  $M$  are the number of rows and columns, respectively than the number  $n$  of the current sample can be represented as  $n = Ml + m$ , where  $l$  is the current row number and  $m$  is the current column number. Moreover, in this case, the current number of an element of the DFT output signal matrix can be read as  $k = Lr + s$ . In this case, the formula of the DFT takes the following form [1]:

$$X(k) = X(s, r) = \sum_{m=0}^{M-1} \sum_{l=0}^{L-1} x(l, m) \cdot W^{(Ml+m)(Lr+s)} = \sum_{m=0}^{M-1} (W^L)^{mr} \cdot \left[ W^{ms} \cdot \sum_{l=0}^{L-1} x(l, m) \cdot (W^M)^{sl} \right] \quad (5)$$

According to the representation (5), the sequence of operations is as follows:

- 1) calculate the  $L$ -point DFTs with the transform kernel  $W^M$  for all columns (computation of the inner sum);
- 2) multiply each element of the result of step 1 by the twiddle factor  $W^{ms}$ ;
- 3) calculate the  $M$ -point DFTs for all rows, resulting from performing of step 1 and step 2, with the transform kernel  $W^L$  (computation of the inner sum).

Changing of the order of summation in (5) on the reverse order leads to the following expression

$$X(s, r) = \sum_{l=0}^{L-1} (W^M)^{ls} \cdot \sum_{m=0}^{M-1} [x(l, m) \cdot W^{ms}] \cdot (W^L)^{rm}. \quad (6)$$

Taking into account (6), the following procedure of calculation of the  $X(k)$  can be used

- multiply the signal samples  $x(l, r)$  by the twiddle factor  $W^{ms}$ ;
- calculate the  $M$ -point DFTs for all rows with the transform kernel  $W^{ms}$  (computation of the inner sum);
- calculate the  $L$ -point DFTs for all columns with the transform kernel  $W^M$ .

Differences in the calculations according to (5) and (6) correspond to the difference between the FFT (the base 2 is used) with the decimation-in-time and decimation-in-frequency, respectively. If the decimation-in-time is used than the multiplication to the twiddle factors is followed by the main operations of the DFT. In the case of the decimation in frequency, the multiplication follows after the operations of the DFT.

The sequence of operations in (5) can be represented in a matrix form, and such representation is suitable for the practical implementation of the algorithm. For a fixed value  $s_0$  (the line number), it can write down

$$X(s_0, r) = \left[ X^T(l, m) \cdot W_{s_0 M}(l) \right]^T \cdot W_{s_0 L}(m, r) = R^T(m, 1) \cdot W_{s_0 L}(m, r) = G_{s_0}(1, r), \quad (7)$$

where  $R(m, l) = X^T(l, m) \cdot W_{S_0M}(l)$ ,  $R(m, l)$  is the column-matrix of dimension  $[M \times 1]$ ,

$X(s_0, r)$  - is the row-matrix of the DFT output signals of dimension  $[1 \times L]$ ,

$W_{S_0L}(m, r) = \left\| \left( W^{Lr+S_0} \right)^m \right\|$  - is the matrix of the twiddle factors of dimension  $[M \times L]$ ,

$r = \overline{0, (L-1)}$ ;  $m = \overline{0, (M-1)}$ ,

$X(l, m) = \|x(l, m)\|$  - is the matrix of values of the input samples of dimension  $[L \times M]$ ,  
 $l = \overline{0, (L-1)}$ ,

$W_{S_0M}(l) = \left\| \left( W^{S_0M} \right)^l \right\|$  - is the column-matrix of the twiddle factors of dimension  $[L \times 1]$ ,

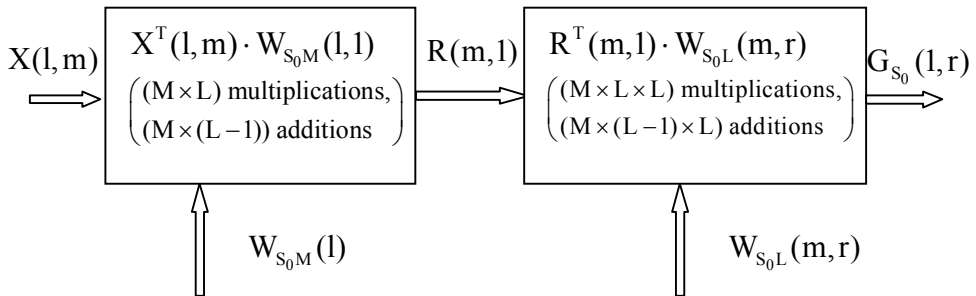
$l = \overline{0, (L-1)}$ .

The sequence of operations in (6) is represented in a matrix form for the fixed value  $s_0$  by the formula

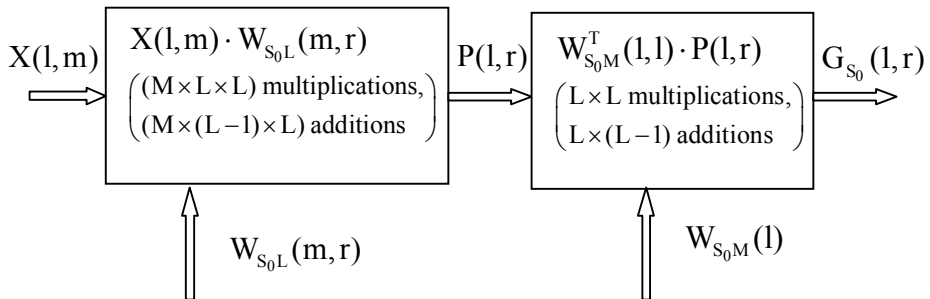
$$X(s_0, r) = W_{S_0M}^T(l) \cdot [X(l, m) \cdot W_{S_0L}(m, r)] = W_{S_0M}^T(l) \cdot P(l, r) = G_{S_0}(l, r), \quad (8)$$

where  $P(l, r) = X(l, m) \cdot W_{S_0L}(m, r)$ ,  $P(l, r)$  is the matrix of dimension  $[L \times L]$ .

According to the expressions (7) and (8), the sequences of operations are presented by Fig. 1 and Fig. 2, respectively.



**Fig.1. The scheme of calculation of the row-matrix of DFT output signals of dimension  $[1 \times L]$  with the decimation-in-time.**



**Fig.2. The scheme of calculation of the row-matrix of DFT output signals of dimension  $[1 \times L]$  with the decimation-in-frequency.**

An FFT representation as a product of the matrices (7) or (8) makes it relatively easy to count the number of elementary operations in the implementation of the FFT, and, what is the most importantly, to identify those operations (that digital information), the result of which can be used at each step of the “sliding” FFT.

The “sliding” or “galloping”  $N$ -point DFT of the input discrete signal  $x(n)$  is given by

$$F(n, k) = \frac{1}{N} \sum_{m=0}^{N-1} s(n-m) \cdot \exp\left(-i \frac{2\pi mk}{N}\right), \quad (9)$$

where  $m, k = 0, 1, \dots, (N-1)$ .

For a fixed number  $n$ , the function  $F(n, k)$  is being the DFT in the variable  $m$  of the interval  $x(n-m)$  of the data stream  $x(n)$ . If  $n = 0, 1, 2, \dots$  than the FFT is a “sliding” FFT. If the step  $\Delta n$  is greater than 2, the FFT is a “galloping” FFT. The function  $F(n, k)$  it is convenient to call the current Fourier spectrum.

Let us schematically consider in a matrix form an offset of the time window containing  $N$  samples, representing the samples by their numbers in the incoming time sequence. For example, if  $N = 16 = 4 \times 4$  and  $\Delta n = 1$  than

1 <sup>st</sup> window				2 <sup>nd</sup> window				3 <sup>rd</sup> window			
1	2	3	4	2	3	4	5	3	4	5	6
5	6	7	8	6	7	8	9	7	8	9	10
9	10	11	12	10	11	12	13	11	12	13	14
13	14	15	16	14	15	16	17	15	16	17	18

**Fig. 3. Representation in a matrix form of the numbers of input time sequence of the “sliding” FFT.**

The columns 2-4 of the first window are the columns 1-3 of the second window, the columns 2-4 of the second window are the columns 1-3 of the third window etc. This means that for each step (for the next time window position) the values  $(M-\Delta n)$  of the  $L$ -point column FFTs ( $M$  is the number of columns,  $L$  is the number of rows) can be used with the previous step. As one can see from Fig. 3, for the “sliding” FFT the data processing of the function  $x(n)$  should be carried out on columns according to the formulae (5) or (7) (see Fig. 1).

Another possible scheme can be realized by using the values of the row FFTs. For instance, if  $N = 16 = 4 \times 4$  and  $\Delta n = 4$  than

1 window				2 window				3 window			
1	2	3	4	5	6	7	8	9	10	11	12
5	6	7	8	9	10	11	12	13	14	15	16
9	10	11	12	13	14	15	16	17	18	19	20
13	14	15	16	17	18	19	20	21	22	23	24

**Fig. 4. Representation in a matrix form of the numbers of input time sequence of the “galloping” FFT with the step  $\Delta n=4$ .**

When the window of information processing is moved than the rows 2-4 of the first window are the rows 1-3 of the second window, the rows 2-4 of the second window are the rows 1-3 of the third window, etc. This means that for each step (for the next position of the time window), the values  $(L-1)$  of the  $M$ -point row DFTs can be used with the previous step. According to Fig. 4, for the “galloping” FFT with the step  $\Delta n = 4$ , the data processing of the function  $x(n)$  should be carried out in rows by using the formulae (6) or (8) (Fig. 2).

Thus, fixing the length  $N$  for a certain time window and a step of displacement  $\Delta n$ , as well as comparing the features of the algorithms (5) and (6) (with the decimation-in-time or decimation-on-frequency, respectively), one can choose (relatively simple) the most high-speed schematic decision of the FFT calculation in a “sliding” window. When the sliding procedures are implemented, the selection decision, which algorithm must be given priority (with processing by rows or columns) should be made depending on the step of sliding. For example, if the step of sliding  $\Delta n = 1$  (see Fig. 3) than it should be selected the algorithms (5) and (7) – the processing by columns. If the step of sliding  $\Delta n = 4$  (see Fig. 4) than it should be selected the algorithms (6) and (8) – the processing by rows.

For the case  $N = 16$ , let us arrange the input values in a matrix of dimension  $4 \times 4$ . In this case  $L = M = 4$ ;  $l = 0, 1, 2, 3$ ;  $m = 0, 1, 2, 3$ ;  $r = 0, 1, 2, 3$ ;  $s = 0, 1, 2, 3$ . The matrices are

$$W_{s_0L}(m, r) = \begin{pmatrix} W^0 & W^{(4+s_0) \cdot 0} & W^{(8+s_0) \cdot 0} & W^{(12+s_0) \cdot 0} \\ W^{S_0 \cdot 1} & W^{(4+s_0) \cdot 1} & W^{(8+s_0) \cdot 1} & W^{(12+s_0) \cdot 1} \\ W^{S_0 \cdot 2} & W^{(4+s_0) \cdot 2} & W^{(8+s_0) \cdot 2} & W^{(12+s_0) \cdot 2} \\ W^{S_0 \cdot 3} & W^{(4+s_0) \cdot 3} & W^{(8+s_0) \cdot 3} & W^{(12+s_0) \cdot 3} \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ W^{S_0} & -j \cdot W^{S_0} & -W^{S_0} & j \cdot W^{S_0} \\ W^{2S_0} & -W^{2S_0} & W^{2S_0} & -W^{2S_0} \\ W^{3S_0} & j \cdot W^{3S_0} & -W^{3S_0} & -j \cdot W^{3S_0} \end{pmatrix}$$

For the various values of  $s_0 = 0, 1, 2, 3$ , the corresponding matrices are

$$W_{0L} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -j & -1 & j \\ 1 & -1 & 1 & -1 \\ 1 & j & -1 & -j \end{pmatrix}, \quad W_{1L} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ e^{-j\frac{\pi}{8}} & -j \cdot e^{-j\frac{\pi}{8}} & -e^{-j\frac{\pi}{8}} & j \cdot e^{-j\frac{\pi}{8}} \\ e^{-j\frac{2\pi}{8}} & -e^{-j\frac{2\pi}{8}} & e^{-j\frac{2\pi}{8}} & -e^{-j\frac{2\pi}{8}} \\ e^{-j\frac{3\pi}{8}} & j \cdot e^{-j\frac{3\pi}{8}} & -e^{-j\frac{3\pi}{8}} & -j \cdot e^{-j\frac{3\pi}{8}} \end{pmatrix},$$

$$W_{2L} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ e^{-j\frac{\pi}{4}} & -j \cdot e^{-j\frac{\pi}{4}} & -e^{-j\frac{\pi}{4}} & j \cdot e^{-j\frac{\pi}{4}} \\ -j & j & -j & j \\ e^{-j\frac{3\pi}{4}} & j \cdot e^{-j\frac{3\pi}{4}} & -e^{-j\frac{3\pi}{4}} & -j \cdot e^{-j\frac{3\pi}{4}} \end{pmatrix},$$

$$W_{3L} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ e^{-j\frac{3\pi}{8}} & -j \cdot e^{-j\frac{3\pi}{8}} & -e^{-j\frac{3\pi}{8}} & j \cdot e^{-j\frac{3\pi}{8}} \\ e^{-j\frac{3\pi}{4}} & -e^{-j\frac{3\pi}{4}} & e^{-j\frac{3\pi}{4}} & -e^{-j\frac{3\pi}{4}} \\ -e^{-j\frac{\pi}{8}} & -j \cdot e^{-j\frac{\pi}{8}} & e^{-j\frac{\pi}{8}} & j \cdot e^{-j\frac{\pi}{8}} \end{pmatrix}.$$

The column-matrix of the twiddle factors  $W_{s_0M}(l) = \left\| \left( W^{S_0M} \right)^l \right\|$  for  $N = 16$  is

$$\left\| \left( W^{S_0M} \right)^l \right\| = \left( W^{S_0M \cdot 0} \quad W^{S_0M \cdot 1} \quad W^{S_0M \cdot 2} \quad W^{S_0M \cdot 3} \right)^T = \left( 1 \quad W^{4S_0} \quad W^{8S_0} \quad W^{12S_0} \right)^T.$$

For the values  $s_0 = 0, 1, 2, 3$ , the corresponding column-matrices are

$$W_{0M} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}, \quad W_{1M} = \begin{pmatrix} 1 \\ -j \\ -1 \\ j \end{pmatrix}, \quad W_{2M} = \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}, \quad W_{3M} = \begin{pmatrix} 1 \\ j \\ -1 \\ -j \end{pmatrix}.$$

The algorithms (5) and (6) suggest a different number of performed operations. The algorithm (5) suggests the  $N$  of the  $L$ -point transforms (sums), the  $N$  of the  $M$ -point transforms, and the  $N$  multiplications by the twiddle factors. In the algorithm (6), it is implemented the  $N$  of the  $L$ -point transforms (sums), the  $N \times L$  of the  $M$ -point transforms, and the  $N \times L$  multiplications by the twiddle factors. More operations of the algorithm (6) can be explained by the fact that the inner sum has more factors than it has in the algorithm (5), and it is a function of three variable parameters instead of two.

## Conclusion

Using a single matrix approach to the FFT algorithm, algorithms to implement operation "sliding" spectral analysis with maximum use of spectral information for the previous position "time window" are developed. Moreover, when the matrix approach is used, algorithm contains the main grouping fragments to efficiently parallelize the computational process on the basis of principle of thinning time or thinning frequency, including for the "sliding" a sequence of discrete oscillations.

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## Voltage regulation as effective method of increased efficiency in power supply systems for food production

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### Abstract

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**Introduction.** In order to improve the efficiency of power supply system for food industry enterprises it is advisable to use voltage regulation.

**Materials and methods.** Voltage regulation is effective method of increased efficiency in power supply systems. Voltage deviation is a priority issue in the design of power supply systems. Used mathematical tools of probability theory, mathematical statistics, and queuing theory.

**Results and discussion.** The ways of improving food production efficiency are studied by the reduction of process losses caused by defective voltage. The way to improve voltage quality is suggested. The use of semiconductor devices eliminates several disadvantages of mechanical switching device (low speed, low resource) and leaves its main advantage, i.e. sinusoidal nature of voltage curve form. The possibility of using semiconductor devices to perform switching without distortion sinusoid in the time of passing zero allows eliminating the major drawback of mechanical switches their discreteness. This allows to create voltage stabilizers of any degree of accuracy, based on the principle of discrete control by switching transformer unsolders without breaking the current and distorting voltage curve. This explains the set of development directions both in this country and abroad aimed at replacement of contactor switch at currently working RUL (regulation under load) devices on thyristor.

**Conclusions.** We recommend to use the results of study at all food industry enterprises to improve energy efficiency.

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## Introduction

Modern power systems are characterized by multi-stage transformation and great length long of various voltages lines. At the change of the load value there also takes place significant change in the voltage that greatly exceeds the allowable limits. In such circumstances, it is impossible to provide admissible voltage mode only by power generators. It is necessary to apply additional regulating devices, moreover, laws of voltage regulation should be established to ensure the most economical conditions in joined work of reactive power sources, power networks and electronic devices.

Hereby the regulation in the high voltage networks, which feed distributing networks, are aimed at improving the feasibility indexes of networks performance by reducing energy losses in them. In distributing networks voltage regulation laws should ensure the optimum voltage mode at consumers' terminals. Voltage value should be determined basing on minimum losses caused by consumers in the case when the voltage at the electronic receivers terminals differs from nominal.

## Materials and methods

Voltage regulation is effective method of increased efficiency in power supply systems. Voltage deviation is a priority issue in the design of power supply systems. It is used mathematical tools of probability theory, mathematical statistics, and queuing theory.

Voltage regulation provides compensation of voltage losses in power supply systems aimed at maintaining a given voltage quality at the electronic receivers terminals (Patent of Ukraine № 7443, *System of regulating voltage and electrical network mode of operation*, Published 15.06.2005).

In general, the voltage at the consumers:

$$U = U_{mrs} \pm E - \frac{Pr + (Q - Q_c)(x_L - x_c)}{U} \quad (1)$$

where  $E$  - additive voltage generated by regulatory devices;

$P$ ,  $Q$  - active and reactive power of consumption;

$Q_c$  - reactive power of compensating devices;

$(x_L - x_c)$  - network reactance,  $r$  - network resistance;

$U_{mrs}$  - main voltage of enterprise reducing substation.

Usually when evaluating the impact of power quality scientists distinguish two components: electromagnetic and technological [1,9]. Electromagnetic component is associated with the change in energy losses at transmission. Electromagnetic component is connected with normally acceptable terms, while the technological component with the maximum acceptable quality parameters.

Reducing power quality is shown in the growth of power and energy losses, reducing equipment life cycle, technological losses that include reducing goods production, lowering product quality, and output of low-quality products. Technological losses make up to 90 ... 92% of all losses and as usually hidden in products cost. Power engineering specialists conceal this matter, technologists usually do not know the causes of process losses [1,3,9].

Voltage deviation is slow smooth change in voltage caused by load changes. It is defined as the difference between the actual and established  $U$  and nominal  $U_N$  of the given network voltage:

$$\delta U = \frac{U - U_N}{U_N} \cdot 100\% \quad (2)$$

Standards are divided into normal acceptable and maximum allowable. Normal values are maintained with a probability of 0.95, i.e. during 95% of the day time PQI should not go beyond the standard. During the rest of the time (5%) rates can be higher [2,3,6,8].

Normal and maximum acceptable value of steady voltage deviation at the points of power consumers' general connection to power network with 0.38 kV and above voltage is equal to  $\pm 5$  and  $\pm 10\%$  of nominal voltage in power network. In the post-accident modes PQI should not go beyond the maximum allowable values [2,3,4].

Voltage deviation of 5% is allowed for industrial customers in the UK and Italy [1,3,9].

Most electronic devices work at other values of voltage deviation, but in this case significant national and economical losses will be tangible [2,5,8].

## Results and discussion

Voltage deviation are caused by the slow process of load changes in the system, they have different effect on the work of individual consumers. In the case of continuous operation of the electric motor at low voltage, in particular at 90% of nominal value, life cycle of motor insulation decreases by 18-20%, which significantly reduces the efficiency of technological mechanisms that triggers this engine [2,3,7,9].

The most stringent requirements to voltage quality are set by electric receivers. Most critical parameter of voltage change is lamp life cycle. The increase of voltage at filament lamp terminals by 6% causes the reduction in life cycle by 50%. For fluorescent lamps this dependence is reflected weaker. However, both raising or lowering of voltage at their terminals is undesirable. In the first case there is an intensive spraying of oxide material from electrodes and overheating ballasts, in the second there happens the change in pressure of mercury vapor in the flask, which reduces the life cycle and unstable ignition. At manufacturing plants with a continuous cycle at voltage deviations at 7 ... 11% there increases demand for lamps in three times [3,6,8].

Reduction of voltage by 1% causes decrease in luminous flux of fluorescent lamps by 1.25%. Reduction of luminous flux, in turn, leads to poor sanitary and hygienic conditions for workers and lowers productivity. For example, double increase of light helped to improve productivity in mechanical workshops by 12% in wool spin workshops by 21%, i.e. additional costs for improving illumination will be repaid and "poor illumination is expensive" [1,3,9].

Productivity:

$$P = \left( 1 - \frac{\lg B_{\min}}{\lg B_r} \right) z_0 \quad (3)$$

where  $B_{\min}$  - minimum illumination according to safety requirements.

$B_r$  - real illumination.

Sensitivity to light production

$$z_0 = \frac{\tau_r - \tau_M}{\tau_M} \quad (4)$$

where  $\tau_r, \tau_m$  – total length of transactions under appropriate conditions of illumination.

Technological losses are determined by the characteristics of particular machines. Automated manufacturing, pumps and others are sensitive to voltage deviations. By 7% voltage reduction technological workflow extends for 40...60% .

Voltage deviation leads to changes in pumps performance. Economic characteristics of pumps are modeled by equation [2,9]

$$C = c\delta U + \kappa(\delta U)^2, \quad (5)$$

where  $c = -87 \cdot 10^{-3}$  UAH/kW · hour;  $\kappa = -345 \cdot 10^{-3}$  UAH/kW · hour.

Voltage fluctuation affects the characteristics of power converters. When the voltage is increased adjustment angle also rises that leads to the reduction of converter power factor.

Power losses in power supply systems at enterprises depend on variations of voltage and are determined by the expression:

$$\Delta P = \beta^2 \Delta P \left( \frac{100}{100+V} \right)^2 + P_{h.N} \left( \frac{100}{100+V} \right)^2, \quad (6)$$

where  $\Delta P, P_{h.N}$  – loading and idling losses at rated voltage respectively;  $V$  – voltage deviation (refer to economic calculations) [1,2,7].

Voltage deviation

$$\delta U_{ed} = \delta U_{mrs} - \Delta U_{mrs \dots ed} + \sum E, \quad (7)$$

where  $\delta U_{ed}$  voltage deviation at electric device clams.

$\delta U_{mrs}$  – deviation on tires 6...10 kV of main reducing substation (MRS).

$\Delta U_{mrs \dots ed}$  – losses of voltage in the power supply system from MRS to electric devise clams.

$\sum E$  – the amount of added pressure that is created by all means of voltage regulation.

Calculation of voltage mode must be carried out for the maximum and minimum load on the daily scheme. The range of voltage deviations:

$$d = \delta U'_{ed} - \delta U''_{ed} = \delta U'_{mrs} - \delta U''_{mrs} - (\Delta U'_{mrs \dots ed} - \Delta U''_{mrs \dots ed}) + \sum E' - \sum E'' \quad (8)$$

To ensure given voltage mode we can use methods evident from the equation:

$\delta U'_{mrs} - \delta U''_{mrs}$  – voltage regulation on tires of MRS.

$\Delta U'_{mrs \dots ed} - \Delta U''_{mrs \dots ed}$  – reduction of electricity voltage losses.

$\sum E' - \sum E''$  – the use of local voltage regulators.

When regulating voltage on tires of MRS voltage mode changes in all power supply system. This method is called centralized control. Reduction of voltage losses. This method is effective, but requires large investments, because its implementation needs the increase

of conductor cross section or laying another line. The use of local regulators [2,9]. This method is very effective and is recommended for routine application.

However, the most promising is the regulation method conducted by means of effecting voltage and reactive power. Hereby the devices of controlling voltage regulator and KC should be interrelated or even mounted in the same block. The need for using regulating devices in the network is determined on the ground of obtaining the best possible predicted voltage losses in high-voltage and low-voltage networks with the allowed voltage deviations at receivers' terminals. Voltage deviation at any point in the network

$$\delta U = \sum E - \sum \Delta U \quad (9)$$

where  $\sum E$  – the algebraic sum of voltage addition generated on the tires of MRS and regulation devices in other networks;

$\sum \Delta U$  – the sum of voltage losses from MRS to network point to which  $\delta U$  is determined.

As can be seen from the expression, introduction to the network extra voltage addition using voltage regulator can reduce the network cost by reducing wires cut [2].

Calculation of voltage deviations in power supply systems is conducted not in absolute units [B], but in relative [%]. Voltage deviation in the characteristic points A (closest) and B (furthest).

$$\begin{aligned} \delta U_A &= \delta U_{mrs} - \Delta U_{L_{HV}} - \Delta U_{T_{TP}} + E_{T_{TP}} \leq \delta U^+ \\ \delta U_B &= \delta U_{mrs} - \Delta U_{L_{HV}} - \Delta U_{T_{TP}} + E_{T_{TP}} - \Delta U_{L_{LV}} - \varepsilon \geq \delta U^- \end{aligned} \quad (10)$$

$\varepsilon$  – size of the dead zone.

Transformers with RUL (regulation under load) and voltage regulators for them are characterized not only by degree of regulation, but also by dead zone, accuracy of regulation and time endurance. By the dead zone we understand some lane of changing voltage at which there is no response of adjusting equipment. The size of the dead zone is determined by the accuracy of regulation. Controller dead zone must be greater than the degree of regulation on the size order of 0.2-0.5%, otherwise the regulator will work unstable with numerous pointless processing. Time endurance of regulators tunes out devices from short-term voltage changes [1,2,7,9].

If automatic voltage regulation the number of switching is 30 - 40 per day or 10950 - 14600 per year. Significant resource of most RUL devices which operate in network is 5000 switches. Examination of devices contacts should be conducted after 5000 switches, it is necessary to lead revision of switcher up to 3 times a year. This should be allowed neither under conditions of safety, no in terms of labor costs. If we take into account that the general equipment level of transformers by RUL devices is from 0 to 36%, reasons that prevent wider deployment and effective use of automatic voltage regulation will become clear. Necessary resource, sufficient for the work of devices during 20-25 years is 200-250 thousand switching, concerning the fact that with decreasing switching current resource increases. Resource of RUL device shall be not less than 500 thousand switching. For testing contacts electrical operation in the same standard 40 thousand switching are provided for reactor devices and 50 thousand for devices with active current limiting resistors. By international standards IEC 20 thousand switching is recommended [2,4,9].

Further improvement of the contact system is the use of vacuum arc extinguishing explosion chambers in combination with high-speed contactors. Due to such combination, and also the fact that arc quenching is carried out in vacuum arc chambers, but not in oil, can increase the resource of switching device from 1 million switching up to 100 thousand switching under the calculated load. Thyristors for voltage regulation turns to be economically justified in the case of the need to achieve a large number (over 300 thousand) switches per year. However, due to its high reliability, possibility of blocks rapid replacement, non-arc and non-spitted switching, use of semiconductors is appropriate for all types of switching devices both existing and fundamentally new [1,5].

The most appropriate is the connection of mechanical and semiconductor devices with the ability to partition functions in order to provide high reliability of device use over an extended period of time and ensuring high power quality and flexibility of control. Such qualities can be achieved by the creation of thyristor-contact switches that have high-speed contactors with lightweight current-limiting footings. This switch can be operated without thyristor unit. With thyristor unit switching of transformer unsolders is done without arc. Additional costs for thyristor block and some design changes of the device are recovered by a number of advantages: the ability to get unlimited lifetime of contact systems that is defined by mechanical durability of the product, no pollution of oil and other details, and also constructive creation of switch outside the transformer tank that allows to have revision of the device without draining oil and thus significantly reduces labor costs for maintenance [1,3,7,9].

## **Conclusions**

Losses reduction can be achieved by adjusting the voltage at each food industry enterprise, as it is impossible to provide admissible voltage mode only by power generators.

At the reduction of power quality electromagnetic and technological losses increase. Electromagnetic power losses occur in the growth of power and energy losses, at the reducing of equipment lifecycle. Technical losses include reduction of products, manufacturing of lower quality products. Technological losses make up to 90 ... 92% of all losses and are usually hidden in the production cost.

Voltage reduction in lamps causes decrease in luminous flux, which in turn leads to the deterioration of sanitary and hygienic conditions for workers and lower productivity. Additional costs to improve illumination are always paid off, and "bad light" is costly.

The most promising is the regulating method based on effecting voltage and reactive power.

The use of thyristors for voltage control turns economically justified if there is the need to achieve a large number (over 300 thousand) switches per year.

Given recommendations deal with voltage regulation at food industry enterprises. Thus, the voltage deviation is one of the most important problems in power supply systems at industrial enterprises. Its solution is a priority in the design of power supply systems.

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## Spectral radiative submodel for 3-D modeling of natural gas combustion

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### Abstract

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**Introduction.** Availability of valid adequate model of methane mild combustion will allow to model and direct of such processes in industrial burners.

**Materials and methods.** Modeling of methane combustion in burners has been carried using FLUENT and CFX software. Absorption coefficient obtained on the basis of “grey” models has been corrected by taking into account the fraction of black body radiation within the bands of triatomic gases in combustion products.

**Result and discussion.** The paper deals with the 3-D modeling of natural gas combustion and, particularly, with the development of submodels will allow to determine radiative characteristics of combustion gases. The analysis of radiative heat transfer has been performed, and a submodel for the determination of mean linear absorption coefficient is presented. This submodel takes into consideration a mean value of combustion gases absorptivity based upon calculation of the spectral fraction of black body irradiation. A CFX model of the methane combustion in the cylindrical burner has been developed. The model incorporates the mentioned above spectral absorptivity submodel. The results of the calculations carried out within the 3-D CFX model were compared with the available in the literature experimental results that had been obtained within the same working parameters and operative condition. The comparison shows a close conformity of the results which proves the validity of the proposed optical submodel for the determination of mean linear absorption coefficients of combustion gases and its applicability for the practical 3-D modeling of the combustion processes.

**Conclusion** The developed model, being incorporated into the whole 3-D model of methane combustion, may be used in engineering calculations and in 3-D modeling of combustion processes.

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## Introduction

When developing the 3-d models of complex mutually regulatory and dependent processes, such as combustion, validation (confirmation of adequacy) of the model is challenging. This is determined firstly, because the direct determination of a certain dominant process and the degree of its influence within the complex group of co-existing processes is impossible. In recent years, along with the widespread usage of 3-d modeling methods, especially within the commercial codes FLUENT and CFX, to studying combustion in industrial and in experimental settings, the projects dedicated to the problems of model validation are becoming more common [1-8].

## Analytical review of the literature and theoretical background

As it is known, the radiant energy transfer equation (RTE) has the form [1, 3, 5]:

$$\frac{dI_\lambda}{ds} = -(K_{a\lambda} + K_{s\lambda})I_\lambda + K_{e\lambda}I_{b\lambda} + \frac{K_{s\lambda}}{4\pi} \int_0^\infty \int_0^{4\pi} \Phi(\vec{s}' - \vec{s}; \lambda' - \lambda) I'_\lambda(\vec{s}') d\Omega' \cdot d\lambda', \quad (1)$$

$I_\lambda; I_{b\lambda}$  – spectral radiation intensity of gas and blackbody emitter, accordingly  
 $K_{a\lambda}; K_{e\lambda}; K_{s\lambda}$  – spectral absorption coefficient, scattering and radiation of medium, respectively, at a wavelength  $\lambda'$ .

All values are taken at a wavelength  $\lambda$ , and they are considered constant within a certain wavelengths band  $\lambda + d\lambda$ ;  $\Phi(\vec{s}' - \vec{s}; \lambda' - \lambda) \cdot I'_\lambda \cdot d\Omega' \cdot d\lambda / 4\pi$  – takes into account the probability that the radiation is within the direction of  $\vec{s}' - \vec{s}$ , at a wavelength  $\lambda'$  in the range of wavelengths  $\lambda' - \lambda$  within a solid angle  $d\Omega'$ .  $-(K_{a\lambda} + K_{s\lambda})I_\lambda$  – determines the attenuation of the radiation intensity, that enters the control volume due to absorption of radiation and scattering of energy, when rays pass a segment.  $I'_\lambda = K_{e\lambda}I_{b\lambda}$  – reflects the intensity of spontaneous radiation by control volume.

It is obvious that integration of such integro-differential equation is not possible without some assumptions. Thus, the assumption of local thermodynamic equilibrium emitting-absorbing medium within considered the equation (1) is generally accepted. In this case, according to the Kirchhoff law for a specific frequency of radiation (wavelength) radiation and absorption coefficients are equal,  $K_{a\lambda} = K_{e\lambda}$ . In relation to the products of combustion, a negligible scattering of incident radiation may be neglected ( $K_{s\lambda} = 0$ ) i.e. double integral in equation (1) can be neglected. Thus, the equation (1) after the integration over the whole wavelength range and under an assumption that  $K_{a\lambda}$  and  $K_{e\lambda}$  are constant over the entire range of wavelengths (K), becomes:

$$\frac{dI}{ds} = -KI + K\left(\sigma_0 \frac{T^4}{\pi}\right), \text{ or the same } - \frac{dI}{ds} = -KI + KI_b \quad (2)$$

$\sigma_0$  – Stefan-Boltzmann constant,

$I_b$  – Blackbody radiation intensity.

Equation (2) is integrated within the control volume  $V$  and within a certain solid angle  $\Delta\Omega_i$  yields and after application of Gauss-Ostrogradsky theorem yields [1]:

$$\int_{\Delta\Omega_i} \int_{\Delta A} I_i(\vec{s}_i \cdot \vec{n}) \cdot dA \cdot d\Omega_i = \int_{\Delta\Omega_i} \int_{\Delta V} [-KI + K(I_b)] \cdot dV \cdot d\Omega_i, \quad (3)$$

where the second integral on the left side of the equation involves the integration within the surface  $\Delta A$  of the selected differential finite volume of the equation [1.2]. In general, equation (3) is a basis for the discretization the RTE.

Within the accepted assumptions, the formal solution of the RTE equation (2) by integration along the ray path within a segment  $0-s$  becomes [6, 7]:

$$I_{0-s} = I_0 \exp\left(\int_0^s -K \cdot ds\right) + \int_0^{s'} KI_b \left[ \exp\left(-\int_{s'}^s K \cdot ds''\right) \right] \cdot ds', \quad (4)$$

where the first term determines the amount of radiation which with the intensity  $I_0$  enters at  $s=0$  control volume and absorbed on route of a length  $s$ . The second - take into account the share of own spontaneous radiation within the control volume of a  $0-s'$  length and absorbed in a further segment within  $s'-s$ . If we assume that the control volume is at a thermodynamic equilibrium state and optical parameters longitudinal distribution within  $0-s$  is gradientless, then (5) becomes:

$$I_s = I_0 e^{-K_s} + \frac{\sigma T^4}{\pi} (1 - e^{-K_s}) \quad (5)$$

On the other hand, equation (5), given as:

$$I_0 - I_s = I_0 (1 - e^{-K_s}) - \frac{\sigma T_g^4}{\pi} (1 - e^{-K_s}), \quad (6)$$

can be interpreted as the ratio between the share of incident radiation, absorbed in the control volume on the length  $s$ , and the part of its own radiation of combustion gases with the temperature  $T_g$ , which leaves the control volume. Thus a connection between surface and linear optical properties is established as follows:

$$\varepsilon_g \equiv \frac{\int_0^\infty I_{b\lambda} \varepsilon \cdot (T, p_i, p_t, \lambda, s) \cdot d\lambda}{\int_0^\infty I_{b\lambda} d\lambda} = \frac{\int_0^\infty I_{b\lambda} [1 - \exp(-K_s)] \cdot d\lambda}{\int_0^\infty I_{b\lambda} d\lambda}. \quad (7)$$

The value of surface absorption coefficient defined as a ratio of radiant energy adsorbed by the control volume to radiant energy adsorbed by perfect blackbody. Apparently, equation (8) is written in the most general terms, as it implies  $\varepsilon$  dependence of all parameters of the modeled domain which, in turn, determine the interaction of photons with gas molecules.

It should be noted that the determination of the optical characteristics of the environment in modeling of complex processes of heat transfer in which the radiation heat transfer is dominant in nature, is an extremely difficult task [5-10]. The data and models presented in the literature - significantly differ. Given the extremely complex nature of the

photon interaction with an absorbing medium, the determination of mean values of absorption coefficient is not clear. For example, in [10] the following mean values of linear absorption coefficients are analyzed and recommended. Equation (9) describes the Rooseland's mean  $K_{Roos}$ , which takes into account the profile of the intensity of the absorption within the spectral bands. Instead, the average linear

$$\frac{1}{K_{Roos}} = \frac{\int_0^{\infty} K_{\lambda}^{-1} \frac{dI_{b\lambda}}{dT} d\lambda}{\int_0^{\infty} \frac{I_{b\lambda}}{dT} d\lambda} \quad (8)$$

Planck's absorption coefficient (10) correlates the total intensity of absorption in all spectral bands, with taking into account variation of  $K_{\lambda}(\lambda)$  within bands, and intensity of blackbody radiation:

$$K_{planck} = \frac{\pi \int_0^{\infty} K_{\lambda} \cdot I_{b\lambda} \cdot d\lambda}{6 \cdot T^4} \quad (9)$$

The average absorption coefficient in terms of Patch [11] correlates proportion of absorbed energy to that, which passes through a layer of gas, and the intensity of radiation passing through a layer of gas,

$$K_{Pat} = \frac{\int_0^{\infty} K_{\lambda} \cdot I_{b\lambda} \cdot e^{-K_{\lambda} \cdot S} d\lambda}{\int_0^{\infty} I_{d\lambda} e^{-K_{\lambda} \cdot S} d\lambda} \quad (10)$$

**The purpose and object of the study.** The study aims to develop a submodel allowing to determine the optical characteristics of combustion products. The modes is intended to be incorporation into the further developed 3-D model of methane combustion in the cylindrical burner.

## Materials and methods

A model allowing to determine optic absorption coefficient of combustion products has been developed. Absorption coefficient obtained on the basis of "grey" models has been corrected by taking into account the fraction of black bode radiation within the bands of triatomic gases in combustion products. Being incorporated into the 3-D mode31 of methane combustion in the experimental cylindrical burner, the developed method allowed to obtain results close to those observed in practice.

## Results and discussion

The radiation submodels that are intended for usage in FLUENT or CFX software for the determination of modeled domain optical characteristics are predominantly based on the "gray" absorption model and its modifications WSGG (weighted sum of gray gases) [11]. Simplified models of spectral absorption are presented in [2, 9, 10]. CFX software package provides the possibility to program a set of absorption bands with the possibility to further account the changes of bands' boundaries with the temperature growth. The coefficient of absorption, which can be programmed either as a constant or a function of temperature, is set the same for each band. If now  $\varepsilon_g$  is interpreted as a share of blackbody radiated energy within a range of wavelengths  $\lambda = 0 \dots \infty$  and further determine the energy radiated by the differential element of gas on n-bands, we get:

$$\varepsilon_g \sigma T^4 = \sum_{i=1}^n \int_{\Omega} \int_{\lambda=i-1}^{\lambda=i} (1 - \exp(-K_{i\lambda}s)) \cdot I_{b\lambda} \cdot \cos\theta \cdot d\Omega \cdot d\lambda;$$

Considering that the adopted model  $K_{i\lambda} = \bar{K}_i$  is a constant within the band and the same for each band, we'll have:

$$\varepsilon_g \sigma T^4 = \pi (1 - \exp(-\bar{K}_i s)) \cdot \sum_{i=1}^n \int_{\lambda=i-1}^{\lambda=i} I_{b\lambda} \cdot d\lambda \quad (11)$$

As  $\pi \frac{\sum_{i=1}^n \int_{\lambda=i-1}^{\lambda=i} I_{b\lambda} \cdot d\lambda}{\sigma T^4}$  is an expression for the Plank blackbody radiation particle  $F(\lambda, T)$ , we obtain the value for determining the emission (absorption) in the spectral bands:

$$\varepsilon_g(T) = (1 - \exp(-\bar{K}_i s)) \cdot F(\lambda, T) \quad (12)$$

Thus, the definition  $\bar{K}_i$  requires the prior calculation of  $\varepsilon_g(T)$  for the available "gray" models and particle spectral irradiance at wavelength bands  $F(\lambda, T)$ , typical for this composition of the combustion products and their molar concentration, pressure and linear typical size of the system.

As it is known [9, 12], the magnitude of the spectral energy flow of black body is based on Planck's function:

$$E_{b\lambda}(T)d\lambda = \frac{2\pi hc^2}{\lambda^5} \cdot \frac{d\lambda}{\exp\left(\frac{hc}{\lambda kT}\right) - 1}, \quad (13)$$

$h$  – Planck's constant,  $6.62617 \cdot 10^{-34}$  J s;

$c$  – speed of light  $-2.998 \cdot 10^8$  m/s;

$k$  – Boltzmann's constant  $1.38 \cdot 10^{-23}$  J/K.

Using the method described in [9], for a fraction of blackbody radiation in the spectral band of wavelengths  $\lambda \dots \infty$ , we get:

$$F(\lambda, T) = \frac{15}{\pi^4} \int_{\frac{c_2}{\lambda T}}^{\infty} \frac{\zeta^3 e^{-\zeta} d\zeta}{1 - e^{-\zeta}}, \quad (14)$$

where  $\zeta = \frac{c_2}{\lambda T}$ ;  $c_2 = \frac{hc}{k} = 14387,69_{MKM} \cdot K$ . Numerical integration of (14) within a spectral band  $\lambda_1 - \lambda_2$  can be done in Mathcad. Also, the numerical result can be obtained by substituting (14) by an infinite series and further representing the difference for the limits of spectral band  $\lambda_1 - \lambda_2$ :

$$F(\lambda_1 - \lambda_2, T) = \frac{15}{\pi^4} \sum_{n=1}^{\infty} \frac{e^{-\frac{nc_2}{\lambda_2 T}}}{n} \left\{ \left( \frac{c_2}{\lambda_2 T} \right)^3 \left[ 1 - e^{-n \frac{c_2}{T} \left( \frac{\Delta\lambda}{\lambda_1 \lambda_2} \right)} \left( \frac{\lambda_1}{\lambda_2} \right)^3 \right] + \frac{3}{n} \left( \frac{c_2}{\lambda_1 T} \right)^2 \left[ 1 - e^{-n \frac{c_2}{T} \left( \frac{\Delta\lambda}{\lambda_1 \lambda_2} \right)} \left( \frac{\lambda_1}{\lambda_2} \right)^2 \right] + \frac{6}{n^2} \left( \frac{c_2}{n^2} \right) \left[ 1 - e^{-n \frac{c_2}{T} \left( \frac{\Delta\lambda}{\lambda_1 \lambda_2} \right)} \cdot \left( \frac{\lambda_1}{\lambda_2} \right) \right] \right\} \quad (15)$$

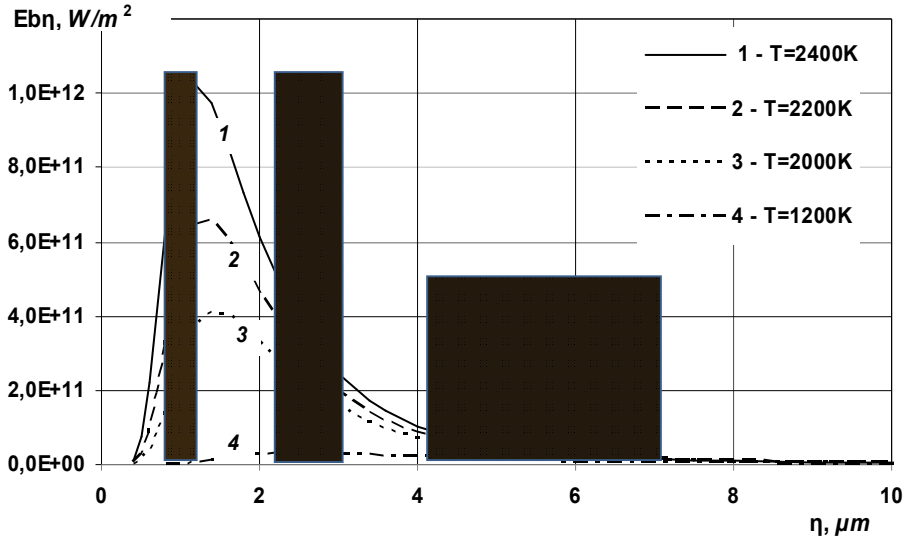
As the calculations and comparison with the results of numerical integration of (14) show, the series (15) converges rapidly for any  $\lambda$ , and at  $T > 600K$ , series converges for  $n > 5$ . Modeling of methane combustion in burners has been carried out at the Department of Thermal Engineering and Refrigeration of National University of Food Technologies using FLUENT and CFX (License №1023420). The values of the coefficients  $\varepsilon(T)$  were calculated by polynomial approximations [6], which were obtained for mixtures of triatomic gases combustion  $CO_2$  and  $H_2O$  at different molar concentrations of the components and variation of the absorbing layer thickness and total pressure by integrating the spectral profiles of absorption of gases HITEMP (USA database of high molecular spectroscopy) and HITRAN (USA database of high resolution molecular absorption).

The bands of radiation-absorption of  $CO_2$  and  $H_2O$  were determined by analyzing data [7, 12, 14].

**Table 1**  
**The absorption bands of combustion products**

Band	CO2			H2O		
	$\lambda$ , mkm	$\lambda$ , mkm	$\Delta\lambda$ , mkm	$\lambda$ , mkm	$\lambda$ , mkm	$\Delta\lambda$ , mkm
1	2,4	3,0	0,6	1,02	1,21	0,19
2	4,0	4,8	0,8	1,32	1,42	0,10
3	12,5	16,5	4,0	1,70	2,00	0,30
4	-	-	-	2,20	3,00	0,80
5	-	-	-	4,80	8,50	3,70
6	-	-	-	12,0	30,0	18,0

Figure 1 shows the results of calculations of spectral blackbody radiation as a function of its temperature  $E_{b\lambda}(\lambda)$  with  $T = var$  (14) in the range of 1200 ... 2400 K, i.e. within a temperature typical for combustion processes of organic fuels.



**Figure 1. Dependence of radiated energy of wavelength**

Three emission-absorption bands (see Table 1) are also presented. As shown in Figure 1 the contribution of the bands within 1.02 ... 1.42 mkm wavelength in total flow of radiation will change significantly with the temperature changes. Thus, if the temperature of the radiator is comparatively low, the share of this band is negligibly small (the curve  $T = 1200$  K). Whereas at  $T = 2000$  K, the fraction of the energy flow transferred on the same band of wavelengths will be significantly higher. As to the wavelength band of 4.0...8.5 microns, which is a merger of bands of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , it is obvious that its share of radiation (absorption) decreases with the temperature increase. This tendency is consistent with the laws of radiation, including Wien's displacement law, which postulates a shift of the maxima of the emitted energy flow towards shorter wavelengths.

The results of calculations (15, 16) for bands listed in Table. 1, are shown in Figure 2. As one can see, the data fully confirm the conclusions mentioned above. Thus, it is possible to note a sharp increase in a share of the short-wave bands. For example, for the shortest waves in band 1.02 ... 1.21 micron the share of the radiated flow in the temperature range 800 K ... 2400 K increases from the 0.0001 to a noticeable 0.1. The longest waves band of 12.0 ... 30 0 mkm have the opposite trend - its share is decreased from 0,108 to 0,008. It is obvious that for such conditions, the influence of individual absorption coefficients within an individual band upon the absorption in the volume of combustion products is not accounted for. In reality, the situation is even more complicated because there is not only a change in the individual bands' absorption coefficients, but there is also a change in the length of bands which is difficult to assess at present. Therefore, the equation (13) determines  $\varepsilon$  - share of blackbody radiation - as a result of total radiation of the bands based on current share of radiation in a given band from the blackbody radiation. On the basis of the data presented in Figures 2 and 3, and  $\varepsilon$  calculations by the correlations given in [6], the linear coefficient of absorption was determined:

$$\bar{K}_i(T) = -\frac{1}{s} \ln \left( 1 - \frac{\varepsilon(T)}{F(\lambda T)} \right) \quad (16)$$

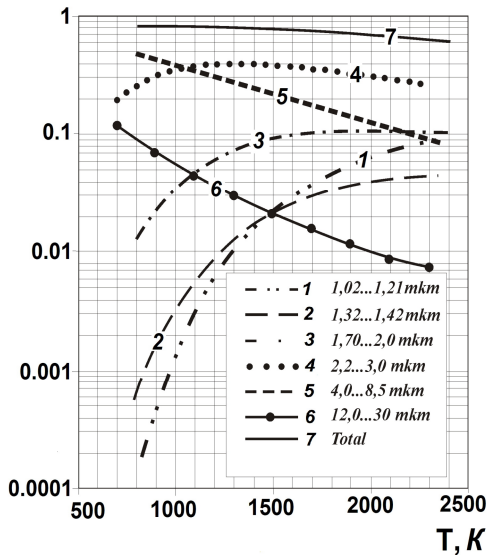


Figure 2. The proportion of blackbody radiation at wavelength bands depending on the temperature

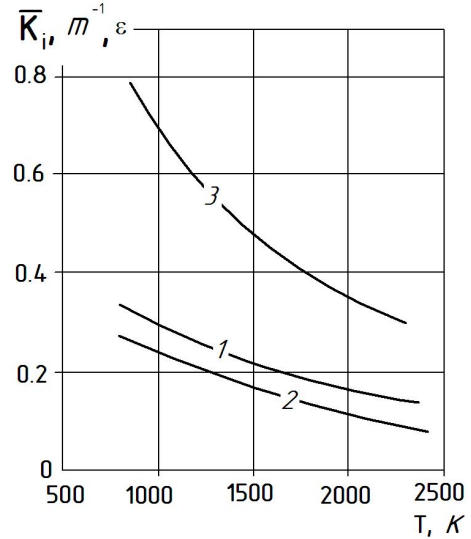


Figure 3. Dependence of optical parameters  $\bar{K}_i(T)$ ,  $\epsilon$  for combustion products of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on temperature: 1 –  $\epsilon_{\text{correct}}$  F(Lamb, T); 2 –  $\epsilon(T)$ ; 3 –  $K(T) m^{-1}$

Validation of the developed model requires the reliable experimental data on the velocity fields, component concentrations, temperature, pressure, etc. Obtaining such data in conditions typical for combustion of organic fuels is an extremely difficult task, primarily, due to the strong gradient fields, when the sizes of probes is comparable to the scale of turbulent fluctuations. As for the measuring of local temperature, in [17-20] it was shown that the usage of thermocouples is associated with the substantial errors. A thermocouple bead itself is a participant of the complex heat transfer. Absorbing heat by means of convection and radiation from the combustion gases, the thermocouple bead radiates in the direction of the cooled walls. It therefore shows not the temperature surrounding flow, but rather its own temperature. Measurements of the components' concentrations using suction probe is also aggravated by errors, since the probe sucks reacting components, which then may react inside the probe lines, despite the "freezing" suction probes may be utilized. This means that at the entrance to measuring device the concentrations of components can be noticeably different from those in the place of probe intake.

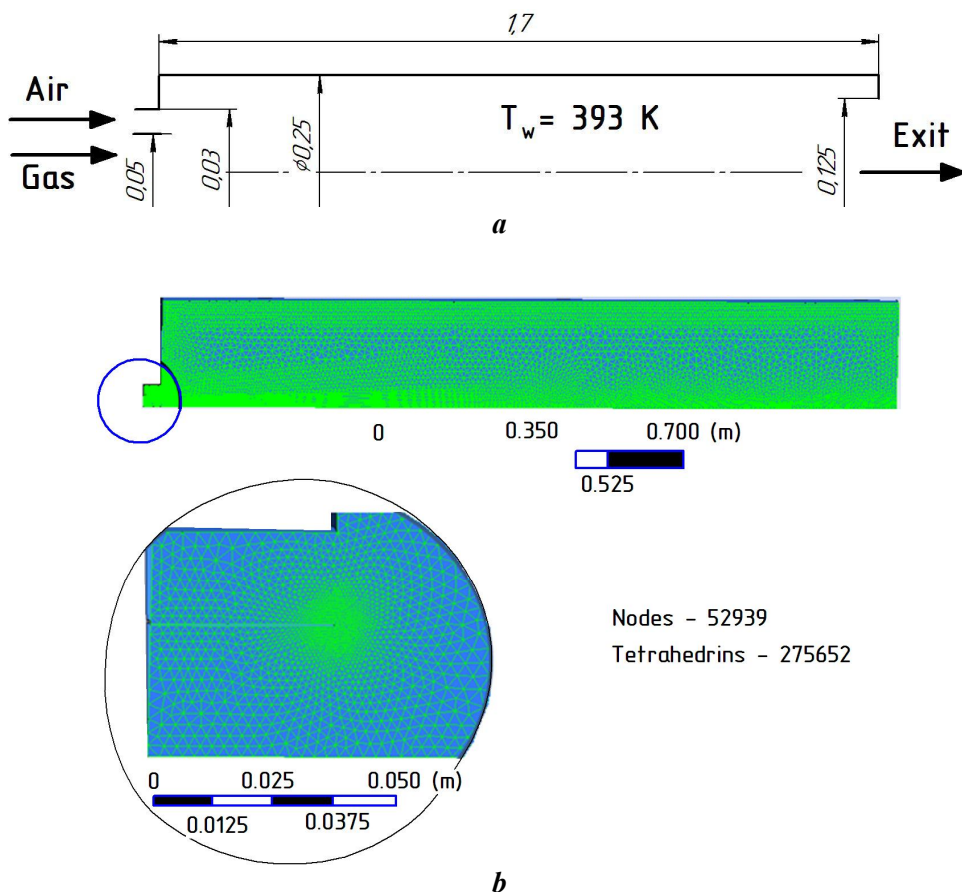
In [11,15,16,] the original data of experimental research of methane mild combustion in a simple cylindrical burner are presented. Measurements of temperature and concentrations of components along the axis of the burner and in the transverse direction in four sections were conducted. Special attention has been paid to the accuracy of temperature measurement. Thus, ultra-thin 55 mm Platinum-Platinum Rhodium thermocouples with double sheathing and suction of combustion products were used. This probes allow, on the one hand, significantly reduce radiant flow from the thermocouple, and on the other - to increase the convective heat transfer between the thermocouple bead and the local environment, thereby bringing the temperature of bead to the local



temperature. The original research data were used as reference for the validation of 3-D models thus developed.

### 3-D CFX model of methane combustion.

Figure 4 (a, b) shows schematic layout, sizes and temperature boundary conditions at the outer wall of the of calculation domain (a) and an unstructured pyramidal grid with the inflation (decreasing size) of cells toward the burner walls and inlets, since in these areas the rise of gradient fields can be predicted.



**Figure 4.**  
*a* – Schematics and size of the burner,  
*b* – Burner's generated grid of the 20° sector.

The mesh was generated in Workbench ANSYS 15 software package, with the usage of highest possible recommended levels of the wall inflation to maximize the precision calculations [20]. As shown in Figure 4 (b), the mesh of the burner 20° sector was generated. This becomes possible because the burner is an axisymmetric object, which, in turn, allows to model the process in the sector, setting the boundary conditions on the lateral faces as symmetry. This method makes it possible to provide the fines fragmentation

in the sector in order to achieve an acceptable calculation time with the available RAM and CPU power. Thus, as it can be seen in Figure 4 (b) generated mesh sector has 52939 nodes at 257 652 triangular pyramids that, when modeling the entire cylindrical burner, would give about 1 million nodes and more than 4.6 million tetrahedrons. Modeling has been performed in CFX-15 commercial code. Pre-processor programming reflected in full compliance the conditions of the experiments [11, 15, 16,].

Under the experiment the flow rates of components were set at: fuel -0.01453 kg / s at 313,15K and air o- 0.1988 kg / s at 323.15 K.

Given the size of inlets, as shown on Figure 4 (a), fuel inlet with a diameter of 0.06 m and a width of the annular aperture of 0.02 m for oxidant inlet, the speed achieved was 7.23 m / s for gas and 36.29 for air. The fuel gas was composed of 90% of methane and 10% of nitrogen and air was composed of 23% of oxygen, 76% of nitrogen and 1% of water vapor, by weight. With such parameters the burner had the heat output of 600 kW thermal and the air flow of  $Re = 18000$ , i.e. the flow was turbulent with the degree of turbulence 5% at the entrance. The kinetics of burning methane in the conditions of turbulence was modeled on the basis of joint mechanisms of chemical kinetics and turbulent dissipation (Finite Rate Chemistry and Eddy Dissipation). Methane combustion was programmed in two-stages:

1.  $CH_4 + 1,5 O_2 = CO + H_2O$ ;
2.  $2CO + O_2 = 2 CO_2$ ;

Arrhenius equation constants for these reactions were taken according to [11, 15, 16]

**Table 2**

**Arrhenius constants and reaction order**

Stage	E, J / mol	A	$\gamma H_2O$	$\gamma CH_4$	$\gamma O_2$	$\gamma CO$
1	$2,03 \cdot 10^8$	$2,8 \cdot 10^{12}$	-	-0,3	1,3	-
2	$1,67 \cdot 10^8$	$2,91 \cdot 10^{12}$	-	-	0,25	1

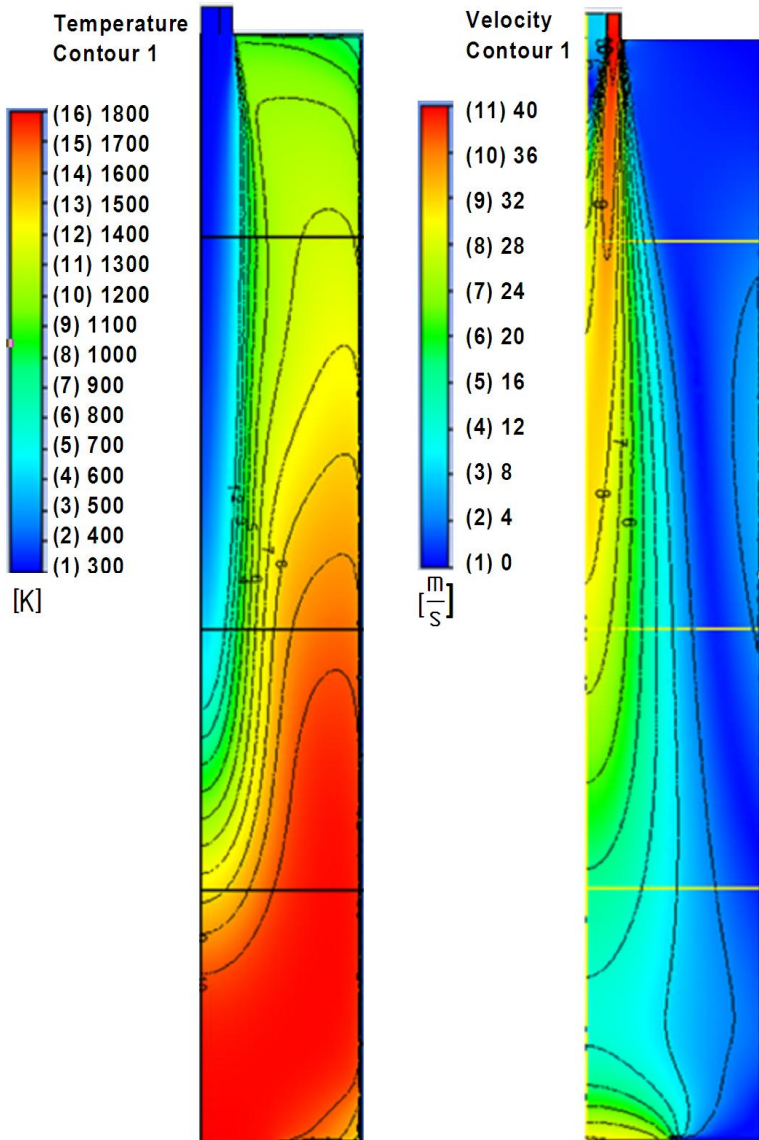
The P-1 model was accepted as a basic model of radiation transfer with optical parameters of the combustion products shown in Figure 3.

Distribution of temperature and speed in the cross section of the burner sector received as a result of model derived as said above are shown in Figure 5.

The comparison of modeling results and experimental data shown in Fig. 6 ... 10.

The calculation results for the model were obtained with the software package CFX Postprocessor and directly imported into the program EXCELL. The experimental points obtained from [11, 15, 16] were digitized and imported into the EXCELL.

As it can be seen from Fig. 6-10, there is a close correspondence between the results of modeling of methane combustion in a laboratory experimental burner to the experimental data of direct measurements of temperature and concentration of components both of fuel and oxidizer as well as products of combustion, which indicates validity of combustion kinetics models, models of turbulent transfer of impulse and the model of optical parameters of combustion products developed within a framework of the present project.



**Figure 5. The fields of temperature and speed in planes of the burner with appropriate scales of contour strips**

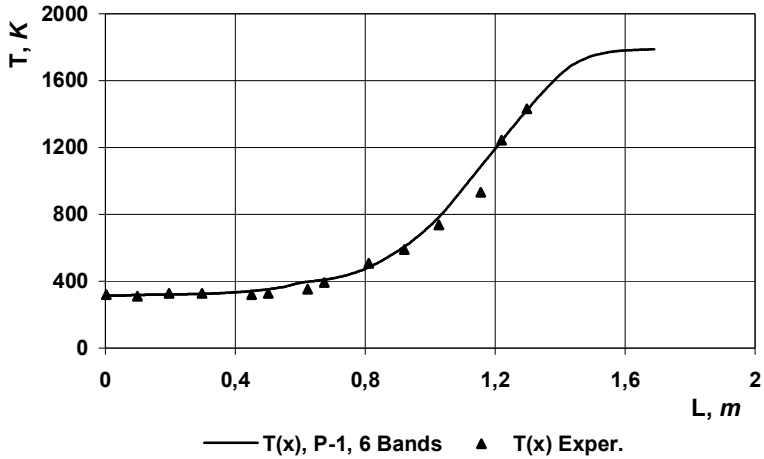


Figure 6. Temperature distribution along the axis of the burner

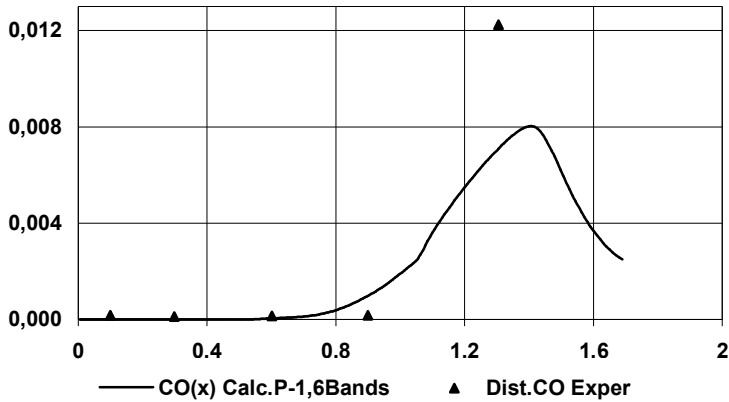


Figure 7. Distribution of CO mass fraction on the axis of flow

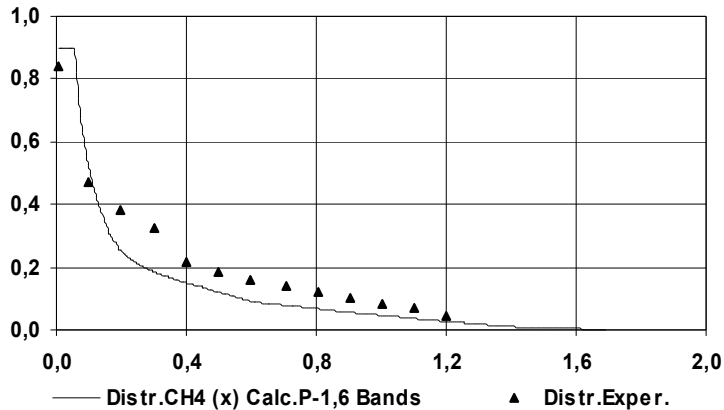


Figure 8. Distribution of CH4 mass fraction of on the axis of flow

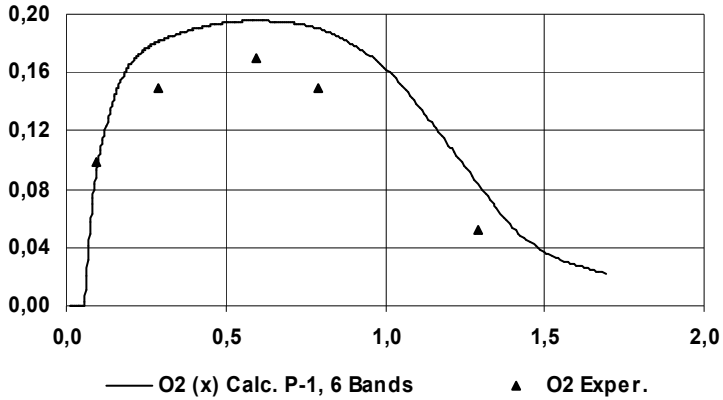


Figure 9. Distribution of the mass fraction of oxygen in the axis of the burner

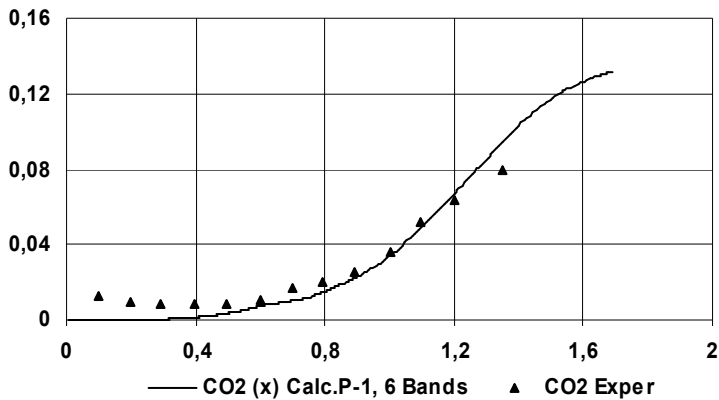


Figure 10. Distribution of the mass fraction of carbon dioxide in the axis of the burner.

## Conclusions

1. The model for the determination of optical characteristics of natural gas combustion products based on a calculation of the fraction of black body radiation within the bands of own radiation of triatomic gases and correction of absorption coefficients obtained within models of "gray" radiation (13.17) was formulated.
2. A 3-D model of methane combustion in a cylindrical burner was developed. The model matches the conditions of experimental study in which the benchmark data were obtained. The data include the distribution of the main components of the process, combustion products along with the temperature and velocity distribution in the burner..

3. The comparison of the calculation results within the developed model of temperature and concentrations of flow component distribution to the experimental data of local measurements was carried out.

Close correspondence between the modeled and experimental data proves that the developed model is adequate to the real process and a submodel for determining the optical parameters of combustion products can be used for computer modeling of combustion processes of fossil fuels at CFX and FLUENT modeling in part of modeling of radiation heat transfer.

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## Improvement of drying process of beer pellet in the fluidized bed apparatus

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### Abstract

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**Introduction.** It is appropriate to model and calculate the processes in the fluidized bed apparatus using computer simulation techniques and experimental studies in order to improve the drying process of beer pellet and develop new structures of dryers.

**Materials and methods.** The process of drying spent grains in the fluidized bed dryer screw. Beer pellet has a thick consistency of rough grinding grain product, a light brown color, sweet flavor and malt smell and it rich in nutrients. Simulation of beer pellet drying was based on the finite element method using the software package Flow Vision and mathematical and statistical methods.

**Results and discussion.** The mathematical model determining allow the coolant pressure in the drying chamber, to depend on the speed and coolant gas distribution device design and optimum conditions of drying installation. Uniform heating and drying the product in the fluidized state at any point of intersection of the drying chamber of screw dryer is achieved through high-quality distribution of coolant above gas distribution device. The expediency of Reynolds criterion definition was proved using semi-empirical interpolation formula derived by V. Goroshko, L. Rosenbaum, and O. Todes. It allows reducing of marker dimensions of the dryer. The design of screw dryers was improved by established under the perforated gas distribution grid profile that provides directional movement of coolant and coolant levels the pressure along the length of the drying chamber.

**Conclusions.** Using the results of research for select the mode of drying in the design phase of drying equipment allows improve drying process beer pellet in the dryer.

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## **Introduction**

The processing, storage and use of wastes of food production has always been a subject of special attention. A large quantity of wastes, a major part of which is beer pellet, is generated in the breweries during the production of beer. This raw by-product is in great demand for animal and poultry fattening as high calorie protein supplement. The problem of beer pellet is virtually absent in winter. But in the summer, the farmers prefer green fodder. That's why a large amount of beer pellet accumulates in the breweries. The term of its storage is limited.

The issue of the recycling of large amount of beer pellet must be solved because many factories pour it into drains thus deteriorating the ecological situation in Ukraine. The 35,000 tons of beer pellet goes annually to waste at the breweries of the average productivity. There are no effective methods of preserving these products except drying. But drying of beer pellet is not used in Ukraine because of the lack of the appropriate equipment.

The drying of beer pellet to the final moisture of 7 ... 10% ensures a long shelf life, making its production and transportation over long distances cost-effective. The solids residue can be used to obtain a great range of products since it contains about 8% of lipids, 26% of proteins, 58% of carbohydrates, minerals, vitamins and other biologically active substances.

Based on the results of the analysis of drying methods, dryers and drying equipment for beer pellet, and according to the research papers on the study of the drying process, it was found that the improvement of the dryer is needed. The improved dryer must be able to dry the product with minimum energy and material consumption. In accordance with these demands the continuous screw dryers was used.

The effect of design features of the improved screw dryer on the drying process of beer pellet was considered and studied.

The development of new methods of bulk stocks drying, designing of small dryers, dryers and in particular improvement of dryers with fluidized (boiling) bed known for its high efficiency and speed drying, simplicity of construction and operation, quality and flexibility of process control of drying is an actual problem.

## **Materials and methods**

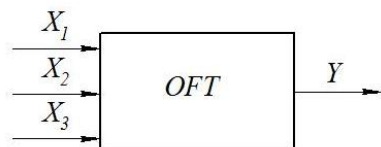
The research material is beer pellet. The pellet formed during filtration congestion as the remainder after separation of the liquid phase - beer wort. Beer pellet has a thick consistency rough grinding grain product, a light brown color, sweet flavor and malt smell. It consists of grain shell, insoluble part of grain. Absolutely dry pellet containing% (wt.), fat – 10; protein – 22; hemicellulose – 35; cellulose – 20; lignin – 10; ashes – 3. Moisture crude pellet is 76...80% (wt.), bulk density of the dried pellet 280...310 kg/m<sup>3</sup>. The dry pellet can be used as biogas, ecological fertilizer use in the manufacture of bread, pasta and sausages.

Mathematical models are often used in addition to physical models when designing new types of equipment and improving existing ones. These calculations allow monitoring the process taking place in the equipment with less time and material resources and optimizing it.

Today the regularity of structural effects arising from the interaction of fluidized (boiling) layer and the degree of influence of these effects on the intensification of heat transfer process are not studied in details. To determine the expediency of using the screw

dryer for beer pellet drying, it is necessary to conduct further research and mathematical modeling.

An important factor to intensify the drying process is uniform distribution of the drying agent under the grid and uniform distribution of fluidized bed of the product. This factor can be investigated using mathematical modeling. The modeling allows optimize the process and obtain numeric values of the parameters that cannot be measured by using the existing devices.



**Fig. 1 The general scheme of mathematical and statistical model:**

$X_1, X_2, X_3$  - input variables  
(factors, regressors),  
 $Y$  - output variable (review)

To establish the optimal technological mode of drying of beer pellet in the screw dryer, it is necessary to develop a mathematical model of the process by the full factorial experiment (Fig. 1).

To achieve the optimum design of the screw dryer it is needed to investigate the coolant distribution and intensity of the drying agent under the gas distribution grid and the pressure on it.

To do this, it is required to create a computer model of the dryer, run a model

and calculation of the drying of beer pellet in the screw dryer.

The procedure of modeling and calculation process includes the following steps:

1. To make a calculation field ("geometry") in CAD and import it into the software package FlowVision.

2. To define the mathematical model.

3. To set the boundary conditions.

4. To set the physical parameters.

5. To set the initial calculation grid.

6. To define the criteria for adaptation of the computational grid.

7. To select the time step of the computational algorithm.

8. To run the calculation.

9. To view the results of the calculation and use the postprocessor capability.

The determination of the Reynolds criteria effects on the calculation of the coolant velocity and as a result, on the size of the dryer (geometry parameters of the grid and the height of the separation space) significantly. Therefore, the choice of the method of Reynolds criteria calculation is one of the main tasks for the developers of the equipment for food enterprises.

The working coolant velocity is determined by the formula:

$$v = \frac{Re \cdot \mu_n}{d \cdot \rho_n} \quad (1)$$

V.D. Goroshko, L.G. Rosenbaum and O.M. Todes obtained the equation for determining the critical velocity of fluidization for Reynolds criterion using the Ergani equation for pressure drop when gas (liquid) moving through the granular layer:

$$Re_1 = \frac{Ar}{150 \cdot \frac{1-\varepsilon}{\varepsilon^3} + \sqrt{\frac{1.75}{\varepsilon^3} \cdot Ar}} \quad (2)$$

Also, it should be noted that Rozhdestvensky O.I. received the refined equation:

$$Re_2 = \frac{Ar}{75 \cdot \frac{1-\varepsilon}{\varepsilon^3} + \sqrt{\left(75 \cdot \frac{1-\varepsilon}{\varepsilon^3}\right)^2 + \frac{1.75}{\varepsilon^3} \cdot Ar}} \quad (3)$$

Also, the authors Goroshko V.D., Rosenbaum L.G. and Todes A.M. offered the generalized semi-empirical interpolation formula for describing the full range of the fluidized bed existence:

$$Re_3 = \frac{Ar \cdot \varepsilon^{4.75}}{18 + 0.61 \cdot \sqrt{Ar \cdot \varepsilon^{4.75}}} \quad (3)$$

where,  $Ar = \frac{g \cdot d^3}{\nu^2} \cdot \frac{\rho_m - \rho_n}{\rho_n}$  – Archimedes criterion;  $\varepsilon$  – porosity of the layer;  $g$  – gravitational acceleration, m/s<sup>2</sup>;  $d$  – average particle size of the product, m;  $\nu$  – velocity of coolant, m/s;  $\rho_m, \rho_n$  – density of the product and coolant (air), kg/m<sup>3</sup>;  $\mu_n$  – viscosity of coolant, Pa·s.

## Results and discussion

The drying process of beer pellet in the screw dryer was simulated. The input parameters that affect the pressure (P, MPa) in the drying chamber are:  $v_p$  – velocity of the coolant in the holes of the gas distribution grid, m/s;  $\phi$  – living section of the grid; C – resistance coefficient of the grid.

According to the full factorial experiment the mathematical model of the pressure in the drying chamber was obtained. It is as follows:

$$P = 2.286 - 0.379 \cdot \frac{v_p - 1.5}{0.5} - 0.614 \cdot \frac{\phi - 0.03}{0.02} - 0.359 \cdot \frac{v_p - 1.5}{0.5} \cdot \frac{\phi - 0.03}{0.02} - 0.701 \cdot \frac{v_p - 1.5}{0.5} \cdot \frac{C - 0.82}{0.08} - 0.541 \cdot \frac{\phi - 0.03}{0.02} \cdot \frac{C - 0.82}{0.08} + 1.186 \cdot \frac{v_p - 1.5}{0.5} \cdot \frac{\phi - 0.03}{0.02} \cdot \frac{C - 0.82}{0.08} \quad (5)$$

The total error of the experiment is  $\Delta = 2,82\%$ .

It should be noted that the construction of the gas distribution grid impacts on the characteristics of the fluidized (boiling) layer in the dryer significantly. The gas distribution grids made in the form of a simple perforated plate, plates with holes closed with caps or cones are widely used.

Fig. 2 shows the effect of the structural characteristics of the gas distribution devices on the fluidized bed characteristics.

As it can be seen from the Fig. 2 the pressure drop is 29% and 41% more when using distributive grids with caps and cones respectively than with perforated grids (porous plates) in the range of critical velocity at the beginning of the fluidization. The decrease of the pressure drop results in the stabilization of fluidized layer, reduction of the hydraulic resistance, the reduction of the costs for creating and maintaining the fluidized bed. It should be also noted that the perforated grids allow obtaining the most uniform layer thus providing the greatest degree of its expansion. They are simple in design, cheap to manufacture and maintain. Therefore, it is recommended to use the perforated grids in the fluidized bed apparatus.

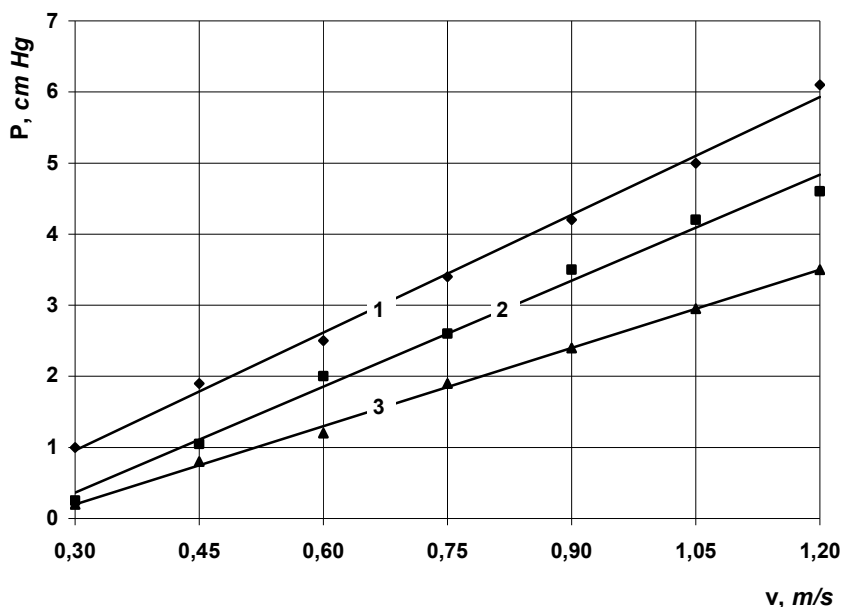


Fig. 2. The variation of the pressure P in a fluidized bed with different distribution devices:  
1 - plate with cones; 2 - plate with caps; 3 - perforated plate.

After the calculations of the Reynolds criterion dependence on the average particle diameter of the device the characteristic curves were obtained (Fig. 3) for the particle diameter from 0,001 m to 0,005 m according to formulas 2 ... 4 using different methods of calculation.

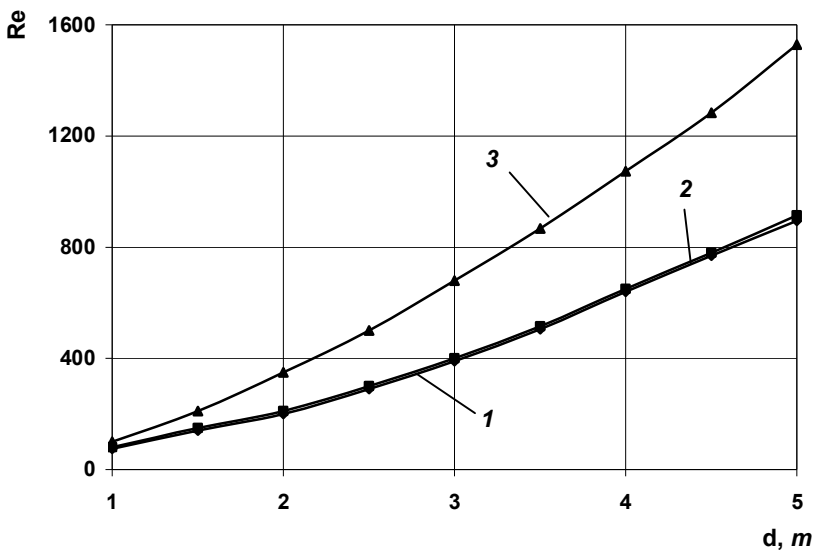
The plot shows that the use of different methods of the Reynolds number calculation results in obtaining the values that differ from each other. For example, the obtained Reynolds number are very high when using the semi-empirical interpolation formula (4) proposed by Goroshko, Rosenbaum and Todes. But the working and critical velocity of the coolant and the diameter of the device will be less in subsequent calculations than when using the other formulas under the same conditions. The two lower curves obtained from formulas (2, 3) give very similar results that are almost identical to each other.

It can be concluded that the proposed methods (2, 3) allow obtaining very similar results, but very small values of the working velocity of the coolant, which in turn leads to the increase of the dimensions of the device and the reduction of the intensity of the heat and mass transfer.

Therefore, it was recommended to calculate the working velocity and dimensions of the equipment using the semi-empirical interpolation formula (4) proposed by O.M. Todes, Goroshko V.D. and Rosenbaum L.G. According to this formula a big value of the working velocity and, consequently, underestimated dimensions of the device can be obtained.

Thus, the choice of the method of Reynolds number calculation is one of the main tasks for the developers of equipment for food companies.

The improved design of the screw dryer was developed after analyzing the study's results of the drying process of beer pellet. The software package Flow Vision was used to model the coolant motion and vector distribution of its velocity, define the pressure in the drying chamber and temperature distribution, observe the nature of air movement and obtain the experimental data.

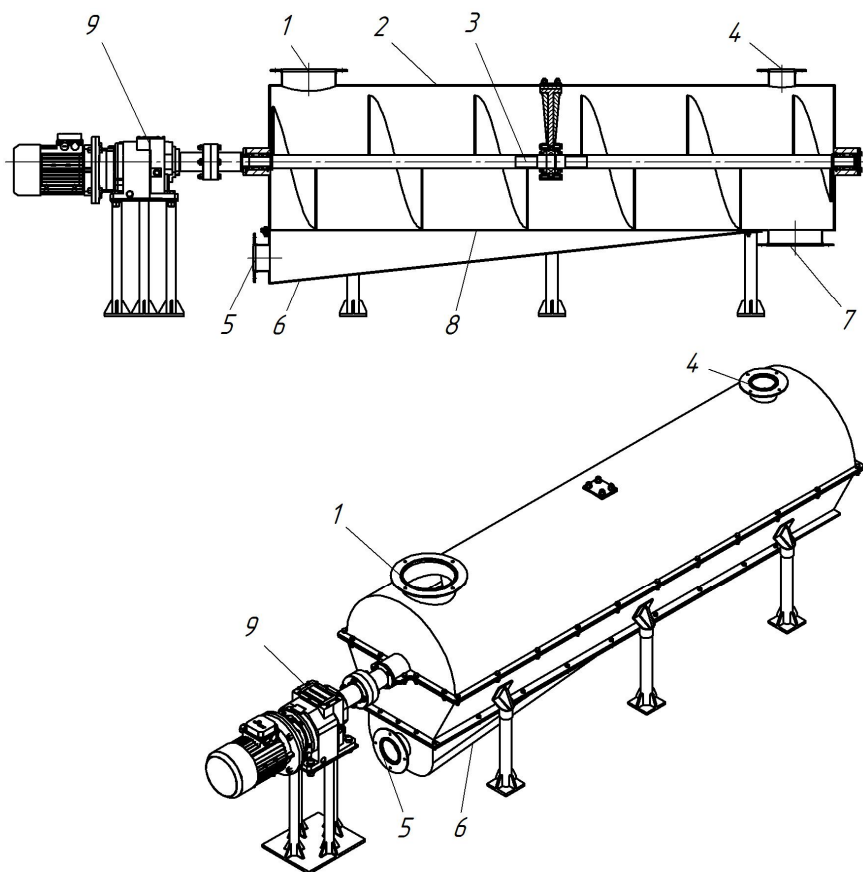


**Fig. 3. The Reynolds criterion vs. particle diameter in the apparatus using different methods of calculation:  
1 – Re<sub>1</sub>; 2 – Re<sub>2</sub>; 3 – Re<sub>3</sub>**

The screw dryer (Fig. 4) performs as follows. The stock is fed into the loading spout 1 of the frame 2 by the feeder while the screw conveyor 3 is rotating and coolant is supplying through the nozzle 5 under the distribution grid 8. The stock is transported from the loading part of the frame 2 to the discharge sleeve 7 by the screw 3. When transporting the stock is stirred intensively and blown by the coolant which creates the fluid (boiling) layer and dries the material. The spent coolant is removed from a frame through the nozzle 4 after rising to the top of the frame 2 above the screw conveyor 3.

The high efficiency of the drying is achieved through the intensive contact of mixing. In addition, the division of the frame 2 by the screw conveyor 3 into the separate sections provides the stability and uniformity of drying. It means that the material cannot come from

the loading 1 to unloading 7 disorderly without sequent drying in each section. Thus, the material is evenly dried reaching the unloading section.



**Fig. 4. The screw dryer for the beer pellet drying:**

- 1 – loading spout; 2 - frame; 3 - screw; 4 - nozzle for coolant removing;
- 5 - nozzle for coolant supplying; 6 - coolant directing profile;
- 7 - nozzle for discharging the dried product; 8 - gas distribution grid; 9 - screw drive

## Conclusions

1. Based on the results of the theoretical and experimental studies the improved design of screw dryer was developed for beer pellet drying. It provides the product drying from the initial moisture content of 80% to the final - 10% with the capacity of 125.4 kg/s.

2. The proposed design of the dryer makes it possible to heat and dry the product uniformly in a fluidized state at any point of the intersection of the drying chamber without disturbance of its properties.

3. The mathematical model was obtained for determining the coolant pressure in the drying chamber. This model allows determining the optimum operating conditions of the dryer.

4. It is recommended to use the semi-empirical interpolation formula by Goroshko V.D., Rosenbaum L.G., Todes O.M. for determining the Reynolds number. This formula will allow reducing the dimensions of the equipment in the subsequent calculations.

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## Description of heat exchange in the similarity theory of vibrating drying process of sunflower

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### Abstract

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**Introduction.** The purpose of research is to develop a criterion equation for calculating the kinetics of drying sunflower seeds in a dryer with vibrating U-eminent container.

**Materials and methods.** The article used the basic tenets of the theory of similarity for heat and mass transfer processes, dynamics of vibration liquefied layer of loose products, methods thermo physical experiment.

**Results.** Done criterion equations in generalized variables of drying sunflower. Due to the small range of measured values and correspondingly large divergence among Stanton, Stanton define generalized numbers with different loading of the container, constructing graphs of the modified Stanton number of vibration from the vibration of the modified Péclet number. Compiled dependency can more accurately take into account the effects of vibration in the implementation of heat and mass transfer processes, including increasing the heat transfer surface, reducing the coefficient of internal friction and viscosity under dry technology environment. Last factors create favorable conditions for the potential reduction of energy consumption in transportation and cooked loose products. The effect of vibration technology is a major factor to adjust the dynamic state of the object processing, particularly in settlement system instability due to energy dissipation in the bulk mass.

**Conclusions.** This equation is recommended for calculating the kinetics of drying sunflower seeds in the range Péclet number  $1.3 < Pe < 2$ , for the degree of loading of the container  $0,33 < \Pi < 0,67$  and with respect to temperature during grain drying and its initial value within  $2,2 < T < 3,4$ .

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## Introduction

The purpose of research is to develop a criterion equation for calculating the kinetics of drying sunflower seeds in a dryer with vibrating U-eminent container.

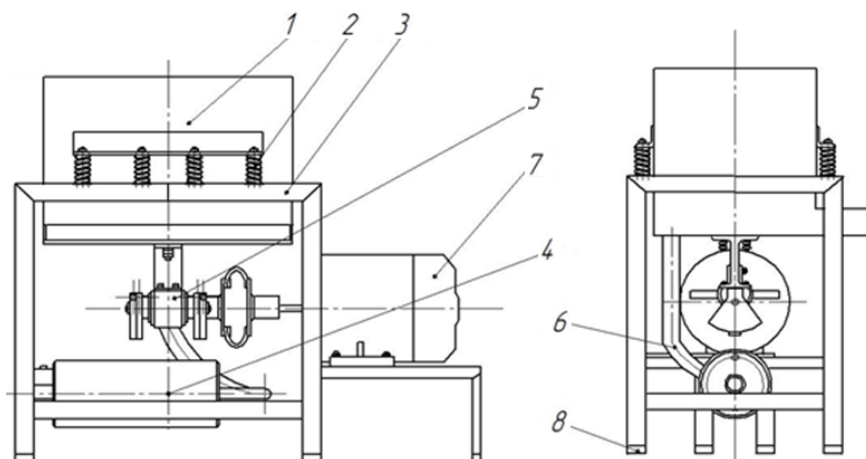
In the study of various physical phenomena used two research methods that allow to obtain quantitative laws. The first method uses experimental study of the specific properties of a single phenomenon, the second - breaking theoretical study of this problem. The advantage of the experimental method of research is the reliability of the results.

## Materials and methods

Investigated materials are freshly sunflower seeds, which after drying process goes on in vegetable oil processing and deposit. Humidity during seed maturation is 15...19%, and the seeds processed – 7%.

Defining constants in the equation of criterion variables generalized process of drying sunflower seeds, based on experimental data base, which was used in the analysis of the similarity theory, statistical processing methods, theory mass transfer and mixing of granular media.

Pseudo-liquefied layer is generated in container drying (Fig. 1) due to vibration vibrations.



**Fig. 1. Single Container experimental vibration dryer**

1 - container; 2 - elastic suspension; 3 - frame; 4 - compressor; 5 - vibrodrive;  
6 - gas pipeline pipe; 7 - motor; 8 - vibrobearings.

## Results and discussion

Pseudo-liquefied layer is generated in container drying (Fig. 1) due to vibration vibrations. Therefore, we can assume that the overall situation in the hydrodynamic device (motion particles) can characterize the total average flow rate and the number that it corresponds to Reynolds number ( $Re$ ).

Therefore, the record number Reynolds should be modified, leading him to the characteristic parameters of the drying process in the vibration field.

Taking as the characteristic size of the system diameter of the machined material (seed) modified vibration (wave) Reynolds number

$$Re_B = \frac{\rho d^2}{\mu} \quad (1)$$

The relationship between convection and molecular processes of heat transfer is characterized Péclet number ( $Pe$ ). Also, this number is the similarity criterion for convective heat transfer processes.

$$Pe_B = Re_B \cdot Sc \quad (2)$$

$$Pe_B = \frac{\rho d^2 f}{\mu} \cdot \frac{V}{D} \quad (3)$$

$$Pe_B = \frac{\rho d^2}{D} \quad (4)$$

$Sc$  – schmidt number

$$Sc = \frac{\nu}{D} \quad (5)$$

Modified vibration Stanton number - the number of similarities

$$St_B = \frac{\beta}{df} \quad (6)$$

$d$  – diameter grains;

$f$  – frequency of vibration;

$D$  – diffusion coefficient (wet-air);

$$D_0 = 0,216 \cdot 10^{-4} \text{ m}^2/\text{c}$$

$\beta$  – mass transfer coefficient during drying

$$M = \beta F (C_H - C_\tau) \quad (7)$$

$M \left[ \frac{\text{M}^3}{\text{c}} \right]$  – moisture removal during drying during the time interval

$F$  – surface area of grain;

$C_H$  – concentration of moisture in the air in terms of air saturation at;

$C_\tau$  – fluid concentrations of moisture in the air

Quest equations in generalized variables takes the form:

$$St_B = A Re_B^n \Pi^m T^k \quad (8)$$

Determination of the constants  $A, n, m, k$  is based on the base of experimental data.

The experiments were conducted by changing:

– production volume in the container:  $\Pi=0,67$ ,  $\Pi=0,5$  та  $\Pi=0,33$

– vibration frequency  $f = 80, 100$  та  $120 \text{ s}^{-1}$ ;

Dimensionless complex parametric loading is determined by the formula:

$$\Pi = \frac{V_3}{V_{II}} \quad (9)$$

$V_3$  – volume loading;

$V_{II}$  – volume container.

The dimensionless temperature:

$$T = \frac{T_3}{T_{II}} \quad (10)$$

$T_3$  – grain temperature during drying;

$T_{II}$  – initial grain temperature

The surface area of grain  $F_{zer}$  determined by the expression:

$$F_{zer} = 4\pi R(l + 3R) \quad (11)$$

$R$  – given radius grains

$$R = \frac{5a + 6b}{60} \quad (12)$$

$a$  – thickness of seed, mm;

$b$  – width of seed, mm

$l$  – length of seed, mm.

Determination of the modified Péclet number vibrating carry the formula (4).

Modified vibration Péclet number when  $f = 80, 100, 120 \text{ s}^{-1}$  will be  $Pe_B = 1, 3, 1, 67, 2$

From formula (7) ratio mass return drying:

$$\beta = \frac{M}{F(C_H - C_\tau)}$$

$M$  – moisture removal during drying during the time interval,  $M^2/c$

$F$  – surface area of grain;

$C_H$  – concentration of moisture in the air in terms of air saturation at;

$C_\tau$  – fluid concentrations of moisture in the air,

$$C_\tau = 13,764 \cdot 10^{-3}$$

Using the i-d chart determines the value  $C_H$  and tabulates. Also in the table puts the calculated values  $M$  and .

Modified vibration Stanton number - the number of similarity is determined by the formula:

$$St_B = \frac{\beta}{df} \quad (13)$$

Due to the small range of measured values and correspondingly large divergence among Stanton, Stanton define generalized numbers with different loading of the container,

constructing graphs of the modified Stanton number of vibration from the vibration of the modified Péclet number. Also, we should consider only download  $\Pi=0,67$  and  $\Pi=0,5$ . When  $\Pi=0,33$  drying process is complicated because of the design of the container and the lack of grain in the container.

To determine the constants  $k$  we plot the dependence modified vibrating numbers Stanton temperature loading of the logarithmic coordinate the grid.

The constants  $k_1$  when loading the container  $\Pi=0,67$  conform  $k_1 = tg73^0 47^1 = 3,37$ , when loading the container  $\Pi=0,5$  constant  $k_2 = tg70^0 = 2,82$  Mean values of constants  $k_1$  та  $k_2$  will correspond to the desired value  $k$

$$k = (k_1 + k_2) / 2 = 3,1$$

To determine the constants  $m$  summarize values  $St_B / T^k$  constructing a graph of  $St_B / T^k$  of the Péclet number in the logarithmic coordinate grid.

Finding data values we plot the dependence  $St_B / T^k$  degree of container load  $\Pi$  and find the required value of the constant  $m$ .

The graph we find  $m = tg42^0 27^1 = 0,91$

To determine the constants  $n$  and  $A$  we plot the dependence  $St_B / T^k \Pi^m$  of the Péclet number in the logarithmic coordinate grid.

The graph we find  $n = tg37^0 2^1 = 0,76$  and  $A = 97,4$

After experimental simulation of the desired equation of one sort

$$St_B = 97,4 Pe_B^{0,76} \Pi^{0,91} T^{3,1} \quad (14)$$

Equation (4) is recommended for calculating the kinetics of drying sunflower seeds in the range  $1.3 < Pe < 2$ ,  $0,33 < \Pi < 0,67$  and  $2,2 < T < 3,4$ .

## Conclusions

The equation is recommended for calculating the kinetics of drying sunflower seeds in the range Péclet number  $1.3 < Pe < 2$ , for the degree of loading of the container  $0,33 < \Pi < 0,67$  and with respect to temperature during grain drying and its initial value within  $2,2 < T < 3,4$ , which makes it possible to justify operating mode settings at vibrodrying.

Implementation vibration pseudo liquid layer drying loose products enables 2.5... 3 times to reduce energy costs and create conditions for uniform distribution and heat dissipation in the mass technological environment.

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## Water-alcohol adsorbing cleaning out of higher alcohols by shungite

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### Abstract

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**Introduction.** The aim of the research work is to increase the quality and safety of high spirits solutions at the expense of using natural adsorbent shungite.

**Materials and methods.** Water-alcohol solutions with 40% concentration and natural adsorbent shungite and being under research here. The solution was passed through the layer of shungite. The content of alcohol was determined by a calorimeter method. Components composition of alcohol was being established with the help of chromatograph “Agileut HP-6890” having a column HP FFAP 50m/032 mm-mkm.

**Results and discussion.** The duration of interaction of water-alcohol solutions with shungite for 20 minutes is optimal in cleaning process. Alcohol is adsorbed more effectively at 0-10°C temperature of the solution decreasing its content from 12.5 to 1.5 mg/dm<sup>3</sup>. Increasing the temperature of water-alcohol solution from 10 to 25°C is followed by increasing the quantity of alcohol from 1.5 to 2 mg/dm<sup>3</sup>. The cleaning process at 25°C of water-alcohol solution is considered irrelevant. Shungite effectively adsorbs alcohol which is harmful for human's health. Hence, the content of n-propanol decreases from 1.71 to 1.35 mg/dm<sup>3</sup>. The content of methanol in water-alcohol solution also decreases from 0.0016 to 0.00035 mg/dm<sup>3</sup>. It can be explained by the fact than shungite has got a developed spongy structure and high adsorbing properties. The existence of shungite deposits, its reasonable price and ecological security gives way to its using for cleaning water-alcohol solutions. The decreased concentration of alcohols in water-alcohol solutions improves orhanoleptic properties of alcoholic drinks and increases their drinking quality.

**Conclusions.** It is highly recommended to use the results of the research for the production of alcohol beverages. This will improve their quality and safety.



## Introduction

High quality rectified ethyl alcohol produced out of food raw material is used to obtain competitive beverages in Ukrainian alcohol production. Rectified alcohol consists of ethanol, water and volatile impurities that significantly affect not only its organoleptic and physico-chemical properties, but also the products produced out of it.

About 200 different contaminants have been identified, but their content does not exceed 0.5-0.6% of the total ethanol [1, 3]. The largest share of them (0.35-0.45 %) are higher alcohols (fusel oil) that provide specific ethanol unpleasant smell and taste and therefore their content is regulated.

The main task of brahorektyfication is to get rectified alcohol with a minimum content of impurities that degrade its quality. However, unwanted impurities remain in ethanol and get into water-alcohol solutions out of which vodka is produced.

Nowadays, alcohol companies in Ukraine use sorption processes to clean water-alcohol out of higher alcohols and other unwanted impurities [4-6]. As sorbents the most commonly used are wood active carbon BAU-A. Active coal contributing to catalytic processes is combustible adsorbent and too expensive.

In recent years, the scientific literature reported about water-alcohol cleaning with natural clay minerals from Ukrainian fields by palygorskite, glauconite, saponins [7-12]. Natural adsorbents were effective absorbing contaminants of alcohol, but during the separation of water-alcohol out of sorbent there is significant hydraulic resistance in the absorber created by a layer clay stuff. Such state of things has become a prerequisite for continuation searching cheap and effective materials that could technologically and economically meet the requirements for adsorbents of alcoholic beverage industry.

A number of researchers for cleaning fruit and vegetable juices and other products used natural carbon containing adsorbent shungit which has high adsorption properties, mechanical stability, and is an environmentally safe sorbent [13].

## Materials and methods

*The object of research* – the process of cleaning water-alcohol solutions.

Materials: water-alcohol solutions, natural sorbent shungite, the quality of cleaning water-alcohol solutions.

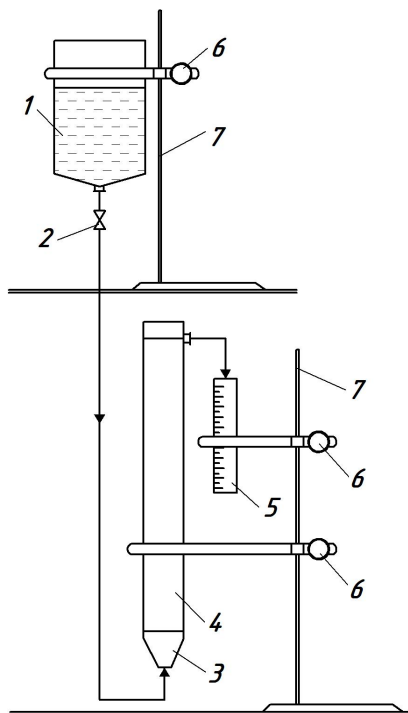
Water-alcohol solution has concentration of 40 volumetric percent. The choice of such concentration is caused by the typical concentration alcohol beverages like horilkas.

Industrial samples of water-alcoholic solution were used in research work.

Shungite. Industrial sample of shungite was used for cleaning water-alcohol solutions. The size of shungite particles is 2 mm.

*Experimental installation.* The laboratory set up has been designed for this purpose and the diagram is shown in fig. 1.

The main element of the installation is the adsorption column 0.45 m high and 0.024 m in diameter. The bottom hole and the layer of the adsorbent column were covered with cloth filter to prevent ingress of powdered Shungite into purified water-alcohol solution. Pretermoactivated shungit was put in the adsorption column in an amount of 230 g. Water-alcohol with concentration of 40% was added to the pressure container 1. Delivery speed of water-alcohol into the column and the length of the contact were regulated by valve 2. Water-alcohol delivery was carried upwards: its first 150 cm<sup>3</sup> returned back to cleaning. Selected samples were analyzed according to the generally accepted physicochemical and chromatographic methods [6].



**Fig. 1 - Laboratory installation for cleaning water-alcohol:**

- 1 - lifting capacity 2 - control valve,
- 3 - adsorption column, 4 - adsorption material, 5 - measuring cylinder,
- 6 – clip, 7 - tripod

were cooled to a temperature of  $20 \pm 0,5$  °C and the optical density of the formed yellow solution was measured immediately for photoelectric filter with a wavelength of light of 540 nm in a cuvette with a thickness of 20 mm facets compared with distilled water.

Chromatographic determination of the content of higher alcohols was performed on chromatograph «Agileut HP-6890», with a column HP FFAP 50 m/032mm-mkm.

#### *Result processing.*

According to the results the calibration curve was constructed by plotting on the horizontal axis the mass concentration of fusel oil, and corresponding values of absorbance of standard solutions were constructed on the vertical axis. Mass concentration of fusel oil in studying water-alcohol was determined by its optical density.

### **Results and discussion**

The results are presented in fig. 2 and 3.

As it can be seen from fig. 2, the content of higher alcohols in water-alcohol in her contact with Shungite falls rapidly during the first 15 minutes, decreasing from 12.5 to 2.0 mg/dm<sup>3</sup>. The following duration of their interaction reduced the number of fusel oil to 0.8 mg/dm<sup>3</sup>.

#### *Preparation of research shungite samples.*

Before using minerals were weighed on laboratory scales and dried in Electrical SESh-1 at a temperature of 140° C for 1.5 h. The dried adsorbent was cooled for 30 minutes in a desiccator and filled in the adsorption column.

Methods of conducting the experiment.

The strength of water-alcohol solutions was checked by areometrical method.

Mass concentration of higher alcohols (except propyl and isopropyl) in water-alcohol was determined by colorimetric method measuring the optical density of the colored solution obtained after interaction of higher alcohols with salicylic aldehyde and concentrated sulfuric acid. Sequence of determination of the mass concentration of higher alcohols with salicylic aldehyde was as follows: 10 cm<sup>3</sup> of concentrated sulfuric acid was slowly added into the tube: 5 cm<sup>3</sup> of researching water-alcohol were put into the first tube, 5 cm<sup>3</sup> of standard solutions containing fusel alcohols 1, 2, 3, 4, 5 mg/dm<sup>3</sup> of anhydrous alcohol were put in the others. 0.7 cm<sup>3</sup> of alcoholic solution of salicylic aldehyde was added into each tube. The tubes were closed with ground-crusts. The contents of the tubes were shaken and placed in a boiling water bath for 10 minutes. The tubes

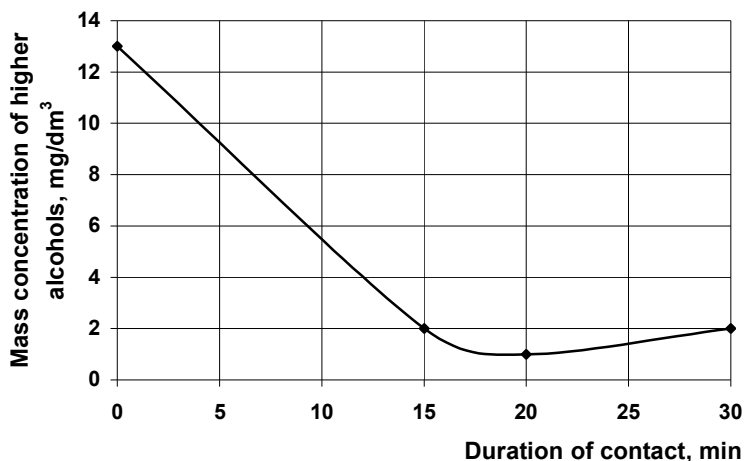


Fig. 2. Duration effect of processing water-alcohol on the content of higher alcohols

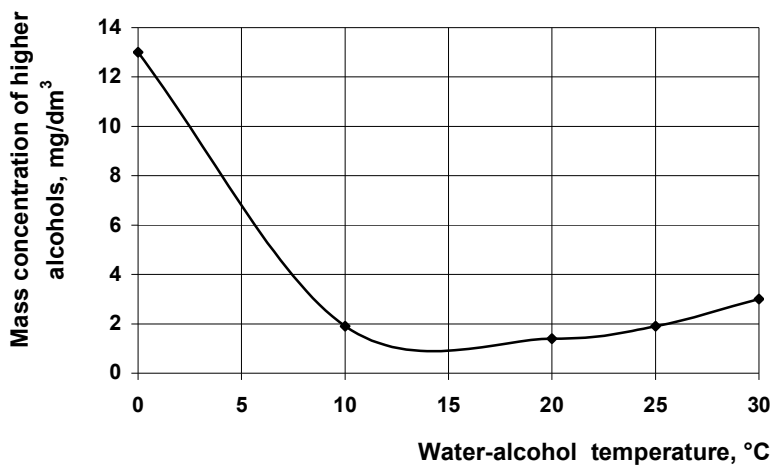


Fig. 3. Effect of water-alcohol temperature on the content of higher alcohols at the duration of its processing by Shungite for 30 min

But with duration increasing of interaction water-alcohol and Shungites to 30 minutes the content of higher alcohols increased to 1.6 mg/dm<sup>3</sup>. This can be explained by the fact that the activity of Shungite during the first 15 minutes is the highest and its active centers were filled with molecules of higher alcohols. Then the presence of oxygen created conditions for passage of catalytic processes accompanied by an increase in the content of impurities. Therefore, it follows that the duration of cleaning water-alcohol by Shungite should not exceed 30 minutes.

From the analysis of the results presented in fig. 3, we see that higher alcohols were adsorbed efficiently at water-alcohol temperatures 0-10 °C. In this temperature range the concentration of higher alcohols in water-alcohol solution decreased from 12.5 to 1.5 mg/dm<sup>3</sup>. When the temperature was risen to 20 °C, an increase in the number of higher

alcohols to 2.0 mg/dm<sup>3</sup> was observed. A further increase in temperature during water-alcohol purification by Shungite helped to rise the number of fusel oil. This can be explained by the fact that the adsorption is an exothermic process accompanied by heat, so the lower temperature processing of water-alcohol by adsorbent, the better fusel oil is adsorbed.

Dynamics of adsorption n-propanol, i-propanol and methanol from water-alcohol by shungite at different duration of its interaction with the adsorbent presents scientific interest, as the presence of the above mentioned additives significantly impairs sensory parameters both water-alcohol and vodkas.

The results of chromatographic analysis of the original and refined water-alcohol by shungite are presented in the table.

**Dynamics of n-propanol, i-propanol, methanol content**

Name of additive	Content of impurities in the original water-alcohol mg/dm <sup>3</sup>	The duration of contact of water-alcohol with Shungite, minutes					
		5	10	15	20	25	30
n-propanol	0.4074	0.2008	0.1853	0.1635	0.1466	0.1267	0.1407
i-propanol	1.7180	1.6624	1.6309	1.5949	1.5843	1.4115	1.3533
methanol	0.0016	0.0004	0.0004	0.0004	0.0004	0.0004	0.00035

It is seen that shungite effectively adsorbs n-propanol at 25 minutes interaction with water-alcohol and reduces its content more than three times. A longer contact with water-alcohol promotes a slight increase in the concentration of n-propanol, indicating the presence of catalytic processes.

Adsorption capacity of shungite for i-propanol appeared to be negligible. Probably, branching of molecule i-propanol makes adsorption difficult.

Methanol is adsorbed by Shungite over interaction time of the adsorbent with water-alcohol. Already after 5 minutes the content of this harmful impurity is reduced four times, remaining at this level for 25 minutes. Thus, a reasonable duration of the sorption process of n-propanol and methanol should be regarded as 25 minutes.

### Conclusions

1. Shungite is an effective sorbent for the removal of higher alcohols out of water-alcohol.
2. When using shungite with particles size 2.0 mm the duration of process should not exceed 25 minutes at water-alcohol temperature 10-25 °C.
3. Shungite effectively adsorbs higher alcohols harmful for people's health. The content of n-propanol decreases from 0.41 to 0.14 mg/dm<sup>3</sup>, i-propanol from 1.71 to 1.35 mg/dm<sup>3</sup> and methanol - four times.

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## Hydrodynamic and diffusive parameters electro-osmotic drying of pectin containing raw materials

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### Abstract

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**Introduction.** When drying pectin content material there is a need to improve the efficiency of removal of bound moisture provided to minimize damage to the cell structure, that can be realized by electro osmotic displacement of water.

**Materials and methods.** It was used analytical methods based on modern concepts of the theory of the surface layer, the main provisions of hydrodynamics and electrodynamics different environments diffusion of fluid motion.

**Results and discussion.** Electro osmotic drying helps to reduce the length of the drying raw material, reducing the loss of biologically active substances. According to research by the equation force electro osmotic diffusion basic laws electro osmotic kinetic motion of the liquid phase of the process, depending on the basic parameters investigated electro hydrodynamic osmotic mass transfer. Given the characteristics pectin content material was obtained dependence for electro kinetic forces pressure liquid diffusion. In implementing the electro osmotic drying raw materials to the designated experimental model of technological industrial machines as intensification factors were selected: vibration centrifugal effect on mass production. Which allows to compress it by passing an electric current; creation vibration suspended state product in the second stage of processing, which allows to significantly increase the effectiveness of the convective flow of coolant. These factors, together with electro osmotic component significantly increase the driving force of the process under study drying.

**Conclusion.** Minimize damage to the structure pectin content raw materials at higher surface mass transfer can be achieved also through the creation vibration liquid layer is implemented in an experimental model of dryer.

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## Introduction

The work is based on the need to improve the efficiency of removal of bound moisture provided to minimize damage to the cell structure, reducing energy consumption in the implementation process. Electro-osmotic pressure accompanying mass transfer inside the capillary liquid on the surface of dispersed highly humid material (pulp). Thus the electrode system should be located tangentially longitudinal surface of the capillary body. The use of low-frequency vibrations through a process promotes both mass compressing the product at electro-osmotic displacement and minimizes damage of material. Thus a combination of vibration action electro-osmotic drying compared with traditional methods of drying plant material, such as convection, infrared, etc., will reduce the duration of the process and improve the quality of raw materials.

The above promotes the use electro-osmotic effect of low-frequency oscillations during seed treatment, water, agricultural production, feeding and other processes [1].

Modern view electro-osmotic drying based on the directed transport of electrolyte ions upon application of an external electric field or own electric field that occurs in materials by electrochemical potential [2].

Patterns electro-osmotic transfer fluid in capillary-porous bodies, as well as through organic membranes cell structure exploring this area of research [3] Antonov R.V. (Kostroma State Agricultural Academy), Ilyukhin S.S. (Moscow State University of Applied Biotechnology), Tkachev R.V. (Moscow State Agrotechnical University im.V.P. Horyachkina) and many others.

## Materials and methods

Investigated materials are beet pulp – the main secondary product of sugar production during the season. He is a capillary-porous colloidal highly humid and body is a complex system like in nature, and structure.

Among the analytical methods for the study were selected main provisions of hydrodynamics and electrodynamics different environments diffusion movement of fluid into the capillary.

## Results and discussion

Statement of the main material spends in the following sequence.

The relative density of electric charge on the inner surface of the cavity material using the expression (1):

$$q = \frac{\varepsilon_0 \varepsilon_M \cdot \xi}{4\pi \cdot \delta} \quad (1)$$

де  $\varepsilon_0 = 8.85 \cdot 10^{-12}$  F/M – absolute permittivity

$\xi$  – electro kinetic potential or zeta - potential, V;

$\varepsilon_M$  – relative permittivity of the material;

$\delta$  – thickness of the electrical double layer;

The thickness of the electrical double layer according to the theory of strong electrolytes (2) can be defined as follows:

$$\delta = \sqrt{\frac{\varepsilon_{ei} \times R \times T}{8\pi \times F^2 \times \sum c_1 \times z^2}} \quad (2)$$

$R = 8.31 \frac{J}{mol \cdot K}$  - gas constant;

$\varepsilon_{ei}$  - relative permittivity of the electrolyte;

$\tau$  - material temperature, K;

$F = 96540$  - Faraday constant;

$C_1$  - concentration of ions of different nature in the electrolyte, mmol / L;

$Z$  - valence ions.

Electro kinetic potential can be determined from the expression (2):

$$\xi = 4\pi\delta \cdot \sigma_q / \varepsilon_{ei} \quad (3)$$

$\sigma$  - surface charge equal to the absolute value of the space charge (1).

Using (3) can be assigned  $\varepsilon_{ei} = 81$ .

The surface charge can be defined as (1):

$$\sigma_q = -\int_0^{\infty} \rho_v dx \quad (4)$$

$\rho_v$  - space charge in the electrolyte solution.

When  $X = \infty$  space charge  $\rho_v = 0$  and provided the electrical double layer electrolytic can assume that the surface charge is equal to the absolute value of the space charge of the electrolyte solution, ie (2):

$$\sigma_q = \rho_v = \sum F \cdot Z_i \cdot C_i \quad (5)$$

Electro-osmotic diffusion of the liquid fraction resulting from the electric field. So in micro capillary, that is limits the distribution of solid and liquid phase occurs electric double layer consisting of positive and negative or so-called potential determining ions, which are on the verge of interfacial separation of "hard surface - Electrolyte." Directly at the surface of the condensed phase adsorbed ions of the same sign; Next is a layer of ions of opposite sign with some distribution diffusion in the normal direction to the interface, creating in this area investigated electro kinetic potential gradient process.

Effects of external electric field leads to a strengthening of the tangential layer of ions with a negative sign along the interface and the corresponding fluid motion. In turn, the movement of fluid under pressure difference also leads to the displacement of ions and of electric current.

Since the conditions of potential flow of the fluid and the corresponding fair Poisson equation:

$$\Delta\phi = -\frac{\rho_q}{\varepsilon} \quad (6)$$

$\Delta\phi$  - Laplace transform;

$\rho_q$  - space charge density.



You can determine the motion of fluids - laminar with a constant coefficient of viscosity  $\eta$ . In the steady state for the system studied is a equation:

$$E\rho_q = \eta \frac{d^2v}{dx^2} \quad (7)$$

$E$  – the electric field.

Under the Poisson equation takes the form  $\rho_q = -\varepsilon \frac{d^2\phi}{dx^2}$  and taking into account (7):

$$-\varepsilon E \frac{d^2\phi}{dx^2} = \eta \frac{d^2v}{dx^2} \quad (8)$$

We perform the integration of equation (8) with the boundary conditions: at

$$x = \infty \quad \frac{dv}{dx} = 0;$$

$$\frac{d\phi}{dx} = 0, \phi = 0; \text{ in the slip plane } \phi = \xi, v = 0.$$

The result is an expression for the velocity electro-osmotic motion:

$$v_{oc} = \frac{\varepsilon \cdot E \cdot \xi}{\eta} \quad (9)$$

The result is an expression for the velocity electro-osmotic motion:

$$V = \frac{\varepsilon \cdot E \cdot \xi \cdot S}{\eta} \quad (10)$$

$S$  – the total cross-sectional area of the capillaries.

For flow caused by hydrostatic pressure drop  $\Delta P$  under conditions of laminar flow, Poiseuille formula can be used:

$$V = \frac{\pi \cdot r_K^4}{8\eta \ell_K} \quad (11)$$

$r_K, \ell_K$  – respectively the radius and length of the capillary.

Osmotic fluid motion, capturing the space charge electric double layer leads to a convection current  $I_K$ , which can be defined as:

$$I_K = \int v_{\Pi} \rho_q df \quad (12)$$

$v_{\Pi}$  – projection of the velocity vector of the fluid on the normal to the element section  $df$ .

Charge transfer leads to a potential difference at the ends of the capillary and under an electric current, which is directed towards the convection and equal to it in size.

Using the differential formulation of Ohm's law  $I = S\sigma_q E$  supply volume flow is determined from the formula:

$$V = \frac{\varepsilon \xi \cdot I_K}{\sigma_K \eta} \quad (13)$$

and the driving force of the process is:

$$\Delta P = \frac{\ell_K \varepsilon \xi \cdot I_K}{S \cdot r_K^2 \sigma_q} \quad (14)$$

The calculation of basic parameters electro-osmotic kinetic process is carried out based on the following assumptions:

- Laminar fluid flow is considered, in which convection current is proportional to the pressure gradient  $\text{grad}P$ , and the electric conduction current - potential gradient  $\text{grad}\phi$  ;
- Radius of curvature of the capillary or pore is much larger than the thickness of the electrical double layer;
- Offset by the value of the surface conductivity of the walls of the capillary, ie the amount of current is determined only by the bulk conductivity of the liquid.

Given the second assumption rises paying potential in the electrical double layer can be considered flat for which:

$$E = \frac{2\pi \cdot q_s}{\varepsilon} \quad (15)$$

Assuming that the sliding layer is sufficiently close to the interface, the potential difference arising from or zeta - potential is:

$$\xi = \frac{2\pi \cdot q_s}{\varepsilon} \delta \quad (16)$$

As a result, the total charge the cylinder unit length and radius  $R_{KP}$  is:

$$q_0 = q_s \cdot S = \frac{\varepsilon \xi \cdot R_{KP}}{\delta} \quad (17)$$

and the value of convection current:

$$I_K = \frac{\varepsilon \xi \cdot R_{KP}}{\delta} v_{CEP} \quad (18)$$

$v_{CEP}$  – average flow rate in the annular space charge layer;

$R_{KP}$  – radius of curvature of the capillary.

When finding the value  $v_{CEP}$  consider that distribution speed laminar fluid flow is parabolic, ie:

$$v_r = v_0 \left( 1 - \left( \frac{r_K}{R_{KP}} \right)^2 \right) \quad (19)$$

$v_0$  – axial velocity.

Integrating value  $v_r$  within the annular layer  $\delta$ , we obtain:

$$v_{CEP} = v_0 \frac{\delta}{R_{KP}} \quad (20)$$

and taking into account the pressure gradient in the process, and that  $R_{KP} = r_k$

$$v_{CEP} = \frac{r_k \delta \Delta P}{4\eta L} \quad (21)$$

Summarizing the analytical study of the current strength of convection  $I_K$  and  $I_{TP}$  conduction are:

$$I_K = \frac{\varepsilon \xi \cdot r_k}{4\eta} \cdot \frac{\Delta P}{L} \quad (22)$$

$$I_{TP} = \pi r_k^2 \sigma_q \frac{\Delta \phi}{L} \quad (23)$$

from which it is clear that

$$\frac{\Delta \phi}{\Delta P} = \frac{\varepsilon \cdot \xi}{4\pi\eta\sigma_q} \quad (24)$$

The relationship between the two studied electro kinetic process or so called value Saksyn, we find, given dependences (13) and (24):

$$\frac{V}{I_{TP}} = \frac{\Delta \phi}{\Delta P} = \frac{\varepsilon \cdot \xi}{4\pi\eta\sigma_q} \quad (25)$$

In terms of electric field strength  $E$  Each layer of liquid  $dx$  moves parallel to the plane of the wall.

Electromotive force balance force of friction between the layers of substances that interact, amounting to:

$$dF = E \rho_q dx \quad (26)$$

Thus each layer of fluid is accelerated by the action of the previous layer and the next layer is inhibited. The magnitude of these forces is proportional to the rate of change of fluid flow  $v$  by changing the distance to the wall is proportional to the derivative  $\frac{dv}{dx}$ .

According to the laws of electrodynamics electrostatic force kinetics is:

$$F_{OC} = qS_o E \quad (27)$$

$S_o$  – total area of the inner surface of the capillaries or pores;

The electric range can be determined from the expression:

$$E = \frac{U}{L} \quad (28)$$

$U$  – voltage of an external electric field, V

The area of the inner surface of the capillary or porous channels are:

$$S_O = 2\pi \cdot r_k \cdot z_k \cdot H \quad (29)$$

$z_k$  – number of capillaries or porous cavities:  $z_k = 0.5h / r_k$

Thus, given the expressions (27), (1), (28), (29) the desired number of force in the electro-osmotic diffusion is:

$$F_{OC} = \frac{\varepsilon_o \varepsilon_M \xi}{4\pi\delta} \cdot 2\pi \cdot r_k \cdot z_k \cdot H \cdot \frac{U}{L} = \frac{\varepsilon_o \varepsilon_M \cdot 4\pi\delta\sigma_q}{2\delta\varepsilon_{en}} \cdot r_k \cdot z_k \cdot H \cdot \frac{U}{L}$$

Given that  $\varepsilon_M = \varepsilon_{en}$  finally obtain:

$$F_{OC} = \frac{2\pi\varepsilon_o\sigma_q \cdot r_k \cdot 0.5 \cdot h \cdot H \cdot U}{L \cdot r_k} = \pi\varepsilon_o\sigma_q \cdot h \cdot H \cdot \frac{U}{L}$$

## Conclusion

1. Electro-osmotic drying promotes intensification of dry plant material, reducing the length of the drying raw material, reducing the loss of biologically active substances.
2. The value electro osmotic pressure depends on the surface charge and geometric dimensions electro osmotic layer.
3. Reducing the damage of the structure pectin content raw materials by increasing the surface mass transfer is achieved by creating a pseudo liquid layer is implemented in an experimental displacer of fluid.

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## Анотації

### Харчові технології

#### Дослідження складу харчових емульгаторів ацилгліцеринної природи методом інфрачервоної спектроскопії

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**Вступ.** Досліджено склад харчових емульгаторів, одержаних із рафінованої соняшникової олії за м'яких умов з метою визначення моно- і діацилгліцеринів жирних кислот і доведення збереження есенціальних біологічно активних компонентів, гальмування процесів термоокиснення.

**Матеріали і методи.** Якісне і кількісне вивчення складу емульгаторів ацилгліцеринної природи, одержаних за м'яких умов (35...40 °С), здійснено із застосуванням інфрачервоної спектроскопії на Фур'є-спектрометрі Perkin-Elmer Spectrum One FTIR Spectrometer методом розчавленої краплі.

**Результати і обговорення.** Вивчено інфрачервоні спектри нових емульгаторів ацилгліцеринної природи і зроблено аналіз характеристичних смуг поглинання, віднесених до відповідних типів валентних і деформаційних коливань триацилгліцеринів (1110 см<sup>-1</sup>, 1173 см<sup>-1</sup>, 1244 см<sup>-1</sup> —  $\nu(\text{C}=\text{O})$  естерів; 1377 см<sup>-1</sup> і 1416 см<sup>-1</sup> —  $\delta_s(\text{C}-\text{H})$  у групах  $-\text{CH}_3$  і  $-\text{CH}_2-$ ; 1736 см<sup>-1</sup> —  $\nu(\text{C}=\text{O})$  естерів; 2855 см<sup>-1</sup> і 2927 см<sup>-1</sup> —  $\nu(\text{C}-\text{H})$  у групах  $-\text{CH}_2-$ ; 3009 см<sup>-1</sup> —  $\nu_{as}(\text{C}-\text{H})$  у групах  $-\text{CH}=\text{CH}-$  у цис-формі), гідроксильних груп моно-, діацилгліцеринів жирних кислот (3435 см<sup>-1</sup>), первинних спиртів (1061 см<sup>-1</sup>).

Доведено наявність у складі нових емульгаторів моно- та діацилгліцеринів жирних кислот і встановлено, що завдяки м'яким умовам їх одержання вони не містять транс-ізомерів і в них збережені ненасичені кислоти у нативній формі.

На підставі визначених спектральних характеристик (пікової інтенсивності, ширини смуги поглинання, площі  $S$ , обмеженої кривою і горизонтальною нульовою лінією) побудовано градувальний графік залежності величини  $S$  від масової частки моно- і діацилгліцеринів у модельних композиціях E471 з рафінованою соняшниковою олією. За допомогою отриманого рівняння прямої визначено сумарний вміст моно- і діацилгліцеринів жирних карбонових кислот у нових харчових емульгаторах, який становить 54,2±1,2%.

**Висновки.** Рекомендовано застосування методу ІЧ-спектроскопії для розв'язання задач кількісного визначення моно- і діацилгліцеринів жирних кислот в емульгаторах ряду ацилгліцеринів E471.

**Ключові слова:** емульгатор, ацилгліцерин, моноацилгліцерин, діацилгліцерин, спектроскопія.

## **Зміни каротину у процесі одержання харчових добавок на основі моркви**

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**Вступ.** Мета досліджень - розробка нових технологічних рішень для більш повного використання корисних властивостей моркви для одержання двох каротиновмісних поліфункціональних харчових добавок у сухому та рідкому вигляді.

**Матеріали і методи.** Використовувались коренеплоди моркви сорту Шантане 2461, морквяний сік, вичавки, порошкоподібний каротиновмісний збагачувач з морквяних вичавок, рідкий концентрований каротиновмісний наповнювач з морквяного соку та продукція комплексної переробки моркви. Хімічний склад усіх зразків визначали згідно з міжнародними стандартами.

**Результати і обговорення.** Запропонована комплексна ресурсозберігаюча технологія переробки моркви з отриманням двох базових каротиновмісних продуктів - сухого та рідкого. Сухий збагачувач "Каротинка", одержаний у виробничих умовах шляхом НВЧ-сушіння морквяних вичавок, відрізняється високим вмістом  $\beta$ -каротину (148,0-154,0 мг/100 г) та клітковини (11 г/100 г). Рідкий наповнювач "Морквяний мед", отриманий на основі морквяного соку (70% сухих речовин), багатий на цукри (52-55 г/100 г),  $\beta$ -каротин (до 11-12 мг/100 г) та пектинові речовини (до 4 г/100 г).

Отриманні продукти піддавали різним технологічним впливам. Можна відзначити порівняно високу стійкість отриманих харчових добавок до різних режимів технологічного процесу.

Апробовано ряд технологій отримання консервованих продуктів з використанням наповнювача "Морквяний мед", а також розроблено нові рецептури кондитерських і хлібобулочних виробів.

**Висновки.** Отриманні каротиновмісні продукти можна використовувати в харчових технологіях як поліфункціональні збагачуючі добавки.

**Ключові слова:** *морква, каротин, окислення, сушіння, концентрування.*

## **Аналіз спектрів дифузного відбивання сухого молока та їх зв'язок з технологічними параметрами**

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**Вступ.** З метою удосконалення продуктів для дитячого харчування проведені дослідження складу сухого молока тварин. Вивчення спектрів дифузного відбивання різних харчових продуктів надає можливість визначати різні фізико-хімічні показники.

**Матеріали і методи.** Інфрачервоні спектри відбивання сухого молока, яке пропонується використовувати у дитячому харчуванні, були досліджені за допомогою приладу «Інфрапід-61». Спектри дифузного відбивання сухих молочних продуктів вивчалися в діапазоні 1330–2370 нм з кроком у 10 нм.

**Результати і обговорення.** Спектри дифузного відбивання сухого молока таких домашніх тварин як кози, кобили та вівці дещо подібні, але на певних довжинах

хвиль існують і суттєві відмінності. Всі досліджувані спектри відбивання кобилячого та козиного сухого молока подібні за своєю формою. Спектр відбивання овечого сухого молока дещо відрізняється від попередніх. Так, на довжині хвилі 1720 нм для всіх трьох спектрів спостерігається мінімум відбивання, але в спектрі кобилячого молока цей екстремум помітно менший. Аналогічні висновки можна зробити, аналізуючи спектри на довжинах хвиль 2310 та 2350 нм. До особливостей слід віднести те, що в інтервалі довжин хвиль 2010–2220 нм спектр відбивання кобилячого сухого молока являє собою монотонну криву з одним екстремумом на довжині хвилі 2110 нм. У той же час у спектрах відбивання овечого та козиного сухого молока проявляються по два екстремуми на довжинах хвиль 2060 та 2170 нм відповідно. Важливим спектральним діапазоном є інтервал довжин хвиль 1480–1500 нм, який відповідає за наявність білків у зразках. Особливо глибокий мінімум характерний для кобилячого молока, яке у своєму хімічному складі має найменшу кількість білків. Вміст білка в козиному та овечому молоці суттєво не відрізняється. Це якісно підтверджують, результати аналізу спектрів відбивання.

**Висновки.** Проведені дослідження дифузних спектрів відбивання у ближньому інфрачервоному діапазоні виявили суттєві відмінності в спектральному розподілі для козиного, овечого та кобилячого сухого молока і дозволили проводити якісний аналіз.

**Ключові слова:** *молоко, спектроскопія, спектр, аналіз.*

### **Кисломолочний напій з антиоксидантними властивостями**

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**Вступ.** Використання пектину та Р-вітамінного комплексу, виділеного з зеленого чаю, як функціональних інгредієнтів кисломолочних напоїв дозволить розширити асортимент, покращити консистенцію готового продукту, а також підвищити його харчову цінність.

**Матеріали і методи.** Оцінку смаку і запаху кисломолочного напою проводили з використанням профільного методу, оснований на тому, що окремі імпульси смаку й запаху, об'єднуючись, дають якісно новий імпульс спільної смакової і запашної характеристики продукту. Дослідження структурно-механічних властивостей зразків проводили на віскозиметрі типу «Реотест-2». Органолептичні показники напоїв оцінювали з використанням п'ятибальної шкали для оцінки виразності відповідного зразка.

**Результати і обговорення.** Найбільш оптимальний профіль з усіх розглянутих дискреторів отримав зразок кисломолочного напою з цитрусовим пектином., що характеризується як гармонійний, кисломолочний, освіжаючий, з вираженим цитрусовим запахом.

Досліджувані зразки кисломолочних напоїв з пектином і Р-вітамінним комплексом відносяться до структурованого твердоподібного тіла, мають найбільшу міцність структурованих зв'язків, їм властива тиксотропія. Найбільш міцний структурований каркас спостерігається у досліджуваному зразку з вмістом фруктового пектину і Р-вітамінного комплексу та з вмістом цитрусового пектину. Максимальна ефективна в'язкість згустків за рахунок пектинових речовин і стабілізаційної дії Р-вітамінного комплексів підвищується порівняно з контролем (кисломолочний продукт без пектину і Р-вітамінного комплексу) в 2,08 та 1,76 раза для кисломолочних згустків із фруктовим та цитрусовим пектином. Поряд із



зростанням в'язкості в зразках спостерігається підвищення міцності структурного каркасу. Напруга зсуву на ділянці повзучості, що визначає зусилля, за якого система починає руйнуватися, у кисломолочних згустків в 2,43...2,53 раза вища, ніж у контрольному зразку.

**Висновки.** За використання фруктового пектину з Р-вітамінним комплексом значно покращується консистенція та структура кисломолочного продукту, а також краще проявляються дискрептори смаку і запаху.

**Ключові слова:** *молоко, пектин, вітамін Р.*

### **Застосування полімерів як носіїв для інкапсуляції олеорезинів спецій**

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**Вступ.** Узагальнено інформацію про олеорезини спецій, різноманітні полімери для їх інкапсуляції та досліджено системи на основі мальтодекстрину та діоксиду кремнію.

**Матеріали і методи.** Матеріалами досліджень були інкапсульовані форми олеорезину розмарину і чорного перцю, інкапсульовані сумішшю мальтодекстрину й діоксиду кремнію. Вивчався вплив концентрації олеорезину у ковбасних виробках на зміну їхніх сенсорних показників і стабільність мікрофлори варених ковбас за стандартними методиками.

**Результати та обговорення.** Здійснено огляд можливих носіїв для олеорезинів. Викладено останні результати досліджень таких носіїв, як вуглеводи, крохмалі, мальтодекстрини, камеді, протеїни. Особливу увагу приділено перевагам і недолікам кожної системи інкапсуляції. Проаналізовано вплив різних комбінацій покривальних матеріалів на ефективність інкапсуляції. Описано дослідження системи носіїв на основі мальтодекстрину та діоксиду кремнію для інкапсуляції олеорезинів перцю чорного й розмарину. Наведено дані про бактеріостатичній дії інкапсульованих форм олеорезинів чорного перцю та розмарину. Отримано комплекс "гість-хазяїн" олеорезину чорного перцю, який інкапсульований у суміші мальтодекстрину (ДЕ15-20) та діоксиду кремнію (А300) у співвідношенні 95:5. Термін придатності варених ковбас був збільшений удвічі у разі використання комплексу "гість-хазяїн" в концентрації 0,2%. Вміст чорного перцю у варених ковбасах становив 0,042%, що не перевищує максимально встановлений рівень.

**Висновки.** Інкапсульована форма олеорезину чорного перцю, а також його комбінування з інкапсульованою формою олеорезину розмарину в процесі зберігання стабілізують значення мікрофлори краще, ніж інкапсульована форма олеорезину розмарину, навіть при збільшенні частки рослинного наповнювача і вологи на основну сировину.

**Ключові слова:** *чорний перець, розмарин, ковбаса, олеорезин, інкапсуляція.*

### **Встановлення рівноважного стану горілок за допомогою <sup>1</sup>Н ЯМР спектроскопії**

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**Вступ.** Метою досліджень є виявлення рівноважного стану гідроксильних протонів етанолу й води у горілках і горілках особливих, вироблених в Україні, за допомогою  $^1\text{H}$  ЯМР спектроскопії.

**Матеріали і методи.** За допомогою мірної піпетки задавали необхідний об'єм (0,3 мл) горілки або горілки особливої. Необхідний для роботи системи LOCK'a - дейтерієвій стабілізації ЯМР спектрометра ацетон-d6 - зовнішній стандарт, який відокремлений від досліджуваної речовини, вносили до ампули у капілярі спеціальної форми; запис спектрів  $^1\text{H}$  ЯМР та обробку даних проводили відповідно до інструкції, що додається до Фур'є ЯМР спектрометра Bruker Avance II (400 MHz).

**Результати і обговорення.** Експериментально визначені елементи встановлення термодинамічної рівноваги гідроксильних протонів етанолу та води у горілках і горілках особливих за допомогою  $^1\text{H}$  ЯМР спектроскопії. Виділено 3 групи зразків з урахуванням рівноваги гідроксильних груп протонів води й етанолу: несталої, перехідної; сталої рівноваги.

Стала рівновага характеризується наявністю в гідроксильній групі об'єданого унітарного сигналу  $\text{EtOH}+\text{H}_2\text{O}$  ( $\delta_{\text{EtOH}+\text{H}_2\text{O}}=4,75\dots4,80$  ppm). Нестала і перехідна рівновага характеризуються наявністю в гідроксильній групі двох роздільних сигналів  $\text{EtOH}$  ( $\delta_{\text{EtOH}}=5,34$  ppm) і  $\text{H}_2\text{O}$  ( $\delta_{\text{H}_2\text{O}}=4,72\dots4,75$  ppm). Характерною їх особливістю є те, що нестала рівновага характеризується наявністю гідроксильного протона етанолу ( $\text{EtOH}$ ), а перехідна рівновага - наявністю ледь помітного сигналу  $\text{EtOH}$ , що характеризує перехід від сталої до несталої рівноваги.

**Висновки.** Існує принципова відмінність поведінки гідроксильних протонів етанолу та води у горілках і горілках особливих. Отримані рівноважні системи дають змогу удосконалити технологічний процес виробництва горілок на лікєро-горілочаних підприємствах для стабілізації якості готової продукції.

**Ключові слова:** *горілка, рівновага, гідроксил, протон,  $^1\text{H}$  ЯМР спектроскопія.*

### **Вплив співвідношення водної та масляної фази емульсій з крохмалем на в'язкість, щільність, розмір часток і мутність системи**

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**Вступ.** Необхідно визначити оптимальне співвідношення водної та масляної фаз, режиму змішування двох фаз, вибір параметрів гомогенізації, при яких отримується стійка емульсійна система.

**Матеріали і методи.** Для досліджень готувались 5 зразків харчових емульсій зі змінною кількістю масляної фази й постійною кількістю стабілізатора (крохмалу) і 5 зразків харчових емульсій з використанням різної кількості крохмалу при постійній кількості масляної фази. В'язкість емульсій визначено на віскозиметрі Brookfield, розмір частинок – на мікроскопі Eastcolight 92012-ES (100x, 250x, 550x, 750h), мутність – на мутнометрі 2100b, щільність - на лабораторному ареометрі.

**Результати і обговорення.** Аналіз емульсій зі змінною кількістю масляної фази і постійною кількістю крохмалу показує, що чим вищий показник масляної фази, тим вища в'язкість, мутність, щільність, рН і розмір часток емульсії, але розмір часток не повинен перевищувати 1 мкм. Аналіз емульсій з використанням різної кількості крохмалу при постійній кількості масляної фази показує, що чим більше крохмалу в складі продукту, тим менші розмір часток емульсії і мутність, що

покращує стабільність емульсійної системи. Збільшення кількості стабілізатора покращує стабільність емульсії, тому що зменшується розмір часток, але мало впливає на мутність. За недостатній кількості стабілізатора утворюються частинки розміром більше 1 мкм, що може призвести до появи «жирового кільця» в системі при зберіганні. Найкращий результат дослідження емульсій з крохмалем полягає в тому, що отримати максимальну кількість часток близько 1 мкм.

**Висновки.** Отримані результати можуть бути основою для створення технології виробництва емульсій як класу харчових продуктів і нових харчових продуктів.

**Ключові слова:** крохмаль, емульсія, гомогенізація.

### **Аномальні властивості у водних розчинах полісахаридів**

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**Вступ.** Дослідження фізико-хімічних властивостей суспензій полісахаридів у широкому інтервалі механічних напруг і температур є важливим при обґрунтуванні технологічних режимів виробництва якісних харчових продуктів.

**Матеріали і методи.** Готували 0,5% суспензії гуарової, ксантанової камеді та камеді річкового дерева, 1,5% суспензію пектину та 10% суспензію нативного картопляного крохмалю у дистильованій воді. Всі суспензії термостатували протягом 30 хв при різних температурах у діапазоні 20-90<sup>0</sup>С.

**Результати і обговорення.** Існування на дифрактограмах досліджуваних полісахаридів широкої смуги свідчить про те, що при розчиненні цих речовин у воді існують або утворюються асоціати молекул полімеру та води. Аналіз мікрофотографій зразків полісахаридів це підтверджує. Проте кристалічність асоціатів камедів проявляється досить слабо, що може бути пов'язане з відмінною від крохмалів структурою самих молекул камедів із розгалуженими боковими ланцюгами. З підвищенням температури водних розчинів полісахаридів вище 40<sup>0</sup> С руйнується квазікристалічна структура комплексів молекул, зростає рухливість молекул розчину, внаслідок чого виникає більш неупорядкована структура. При цьому повинна збільшуватися густина розчину, що викликає підвищення його в'язкості до температури 40<sup>0</sup> С, вище якої в'язкість починає зменшуватися. Таку аномальну поведінку розчинів можна пояснити поліморфними перетвореннями в діапазоні температур 35-55<sup>0</sup> С самих молекул полісахаридів при збільшенні свободи рухів, що підтверджується існуванням екзотермічного піку на кривих диференціальної скануючої калориметрії.

**Висновок.** У результаті поліморфних перетворень збільшується активність молекул полісахаридів у міжмолекулярних взаємодіях.

**Ключові слова:** полісахарид, крохмаль, квазікристал, суспензія.

### Вплив часткового гідролізу на екстрагування білків із соняшникового шроту

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**Вступ.** Досліджено вплив ступеня гідролізу білків за наявності нейтральної протеази *Bacillus subtilis* на процес екстрагування білків із соняшникового шроту. Проаналізовано кореляцію між ступенем гідролізу білків та ефективністю їх екстрагування.

**Матеріали і методи.** Ступінь гідролізу білків визначали як збільшення концентрації білків, розчинних у трихлороцтовій кислоті порівняно з контрольними зразками. Концентрацію білків в екстрактах визначали фотометрично.

**Результати і обговорення.** Визначення концентрації білків в одержаних екстрактах показало, що основна частина білків екстрагувалась протягом перших 20 хвилин. Концентрація білків в екстрактах, одержаних за наявності протеази, була приблизно вдвічі вищою порівняно з контрольними зразками. За невисокого співвідношення фермент: субстрат ступінь гідролізу білків був досить низьким і знаходився в межах від 3,5 % до 5,2 %. Із збільшенням співвідношення фермент: субстрат ступінь гідролізу зростав і досягав 9,0-9,5 % протягом 40-60 хвилин. Такий рівень гідролізу білків прийнятний для удосконалення функціональних властивостей білків, в той час як більш високий рівень гідролізу спричиняє втрату функціональності білків. Отже, ступінь гідролізу білків залежав від співвідношення фермент: субстрат і від тривалості реакції.

Одержана нелінійна модель для оцінки ефективності екстрагування білків як функції від співвідношення фермент: субстрат і від тривалості. Дана модель охоплює 92,81% одержаних експериментальних даних і добре апроксимує одержані результати.

Існує досить висока кореляція ( $r=0,69$ ) між концентрацією білків в екстрактах і ступенем гідролізу білків.

**Висновки.** Частковий гідроліз білків соняшникового шроту нейтральною протеазою збільшував концентрацію білків в екстрактах. Одержана модель може бути використана для прогнозування ступеня гідролізу білків протягом екстрагування за наявності протеолітичних ферментів, а також їх функціональних властивостей.

**Ключові слова:** соняшник, білок, протеаза, гідролізата.

### Збагачення харчових продуктів есенціальними мікроелементами і безпека життя людини: огляд літератури

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**Вступ.** Детальне дослідження взаємодій мікроелементів (Mn, Fe, Cu, Se, Zn, I тощо) в організмі людини дозволяє вирішити низку проблем, пов'язаних із запобіганням і лікуванням хвороб, викликаних дисбалансом мікроелементів.

**Матеріали і методи.** Проаналізована сучасна література про принципи збагачення харчових продуктів мікроелементами. Розглядалися такі питання, як гостра токсичність, значення, біологічна роль і розлади, викликані браком цих мікроелементів.

**Результати і обговорення.** Збагачення мікроелементами необхідно ретельно контролювати, зважаючи на токсичний ефект, який може бути викликаний передозуванням цих елементів.

Вважається, що зростання споживання Zn з 5 до 20 мг на день у раціоні харчуванні людини необхідно компенсувати збільшенням в 16 разів вживання Cu з метою збереження балансу. Згідно з експериментальними дослідженнями, зростання концентрації кожного з цих мікроелементів призводить до зменшення біодоступності кожного з них. Есенційні мікроелементи (Mn, Fe, Cu, Se, Zn, I тощо) є життєво необхідними для підтримання функціональності організму людини. Дефіцит будь-якого з цих елементів призводить до небажаних патологічних проявів, що може бути відтерміновано шляхом адекватного збагачення харчових продуктів.

Одночасне засвоєння есенційних мікроелементів може поглиблювати конкуренцію між ними, починаючи з кишечника і закінчуючи специфічними взаємодіями з білками, лігандами тощо. Взаємодія між мікроелементами може бути як синергічною, так і антагонічною.

**Висновки.** З'ясовано, що найбільш важливими мікроелементами для організму людини і, відповідно, для збагачення харчових продуктів, зокрема хлібопекарських, є Fe, Zn, I та Se.

**Ключові слова:** мікроелемент, цинк, збагачення, дефіцит, токсичність.

## Біотехнологія, мікробіологія

### Вплив апіпродуктів на структурно-механічні і фізико-хімічні властивості йогурту

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**Вступ.** Запропоновано підвищувати біологічну та пробіотичну цінність йогурту додаванням продуктів бджільництва. Визначено вплив цих продуктів на споживчі характеристики йогурту.

**Матеріали і методи.** Матеріали, що використовувалися: нормалізоване молоко, сухі бактеріальні закваски сублімаційного сушіння, мед акації, маточне молочко, пилік. Відбір, підготовка та випробування проводилися за допомогою стандартних методів аналізу. Реологічні параметри було визначено з використанням ротаційних віскозиметрів. Ступінь синерезиса була визначена шляхом фільтрації, вологоутримуюча здатність – шляхом центрифугування. Для визначення відносної в'язкості використовували віскозиметр витікання.

**Результати і обговорення.** Вивчення ефективної в'язкості зразків показало, що додавання меду йогурту в кількості 5% збільшує ефективну в'язкість за незначного руйнування згустку на  $28 \pm 1\%$  і зменшує – за суттєвого руйнування на  $72,5 \pm 2, 5\%$ .

Зразки з медом і маточним молочком руйнувалися найшвидше і мали найвищий індекс плинності – 0,451, але їхня тиксотропна здатність була вищою, ніж у контрольній групі. Внесення в йогурт комплексної добавки меду, маточного молочка і пилку стабілізує в'язкість і прискорює відновлення його структури після руйнування. Це допоможе поліпшити консистенцію після розливу за резервуарного способу виробництва.

Найменша стійкість до вологовіддачі була у зразків із сумішшю меду і маточного молочка – синерезис = 42 мл, ВУЗ = 52%. Найвища – з 5% меду (39 мл), і ВУЗ - 55% відповідно. Зразок, який містив 5% меду, 0,2% маточного молочка та 0,2% пилку мав не найкращі синеретичні властивості серед проб йогурту, але за всіма показниками перевищував контрольний. Титрована кислотність зразків йогурту з 5% меду протягом дев'яти днів наростала швидше порівняно з контрольним та іншими досліджуваними зразками. На шосту добу зберігання вона склала більше 150 °Т, що вище за допустиму норму на 10°Т.

**Висновки.** Кращі показники мав йогурт, містив комбіновану добавку з апіпродуктів (мед, маточне молочко, пилка - 5%, 0,2 і 0,15% відповідно).

**Ключові слова:** мед, бджільництво, йогурт.

## Автоматизація технологічних процесів

### Алгоритми швидкого перетворення Фур'є в задачах спектральної обробки сигналів у системах реального часу

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**Вступ.** Розглянуто алгоритми реалізації швидкого перетворення Фур'є в системах цифрової фільтрації сигналів, які дозволяють скоротити обсяг обчислень і час обробки "ковзної" послідовності дискретних коливань, що "рухається в часі".

**Матеріали і методи.** Використано єдиний матричний підхід до алгоритмів швидкого дискретного перетворення Фур'є.

**Результати і обговорення.** Дискретне перетворення Фур'є кінчної послідовності відліків задається в комплексній матричній формі, що дає змогу визначити структуру повного розпаралелення процесу спектральної обробки за принципом розрідження по часу чи розрідження по частоті для "ковзної" послідовності дискретних коливань. Розроблено алгоритми, що дозволяють реалізувати операцію "ковзного" спектрального аналізу з максимальним використанням цифрової інформації про спектр для попереднього положення "вікна часу". Крім того, завдяки матричній формі перетворень в алгоритмі згруповано основні фрагменти для ефективного розпаралелення обчислювального процесу спектральної обробки за принципом розрідження по часу чи розрідження по частоті, в тому числі для "ковзної" послідовності дискретних коливань. Для прикладу обчислені значення «повертаючих множників» для дискретного перетворення Фур'є – перетворення послідовності 16 відліків радіолокаційного сигналу з «кроком ковзання»  $\Delta N=4$ . Для 16 відліків наступної «ковзної» послідовності 12 з 16 вихідних значень з модуля обробки не перераховуються (2-4 рядки по 4 елементи першого «вікна» стають 1-3 рядками другого «вікна», 2-4 рядки другого «вікна» стають 1-3

рядками третього «вікна» тощо), і тільки 4 з 16 потрібно обчислювати на кожному кроці «ковзання».

**Висновки.** Запропоновані алгоритми суттєво зменшують обсяги обчислень і можуть використовуватись, наприклад, в автоматизованих системах обробки радіолокаційних сигналів у реальному часі.

**Ключові слова:** алгоритм, радіолокація, сигнал, швидке перетворення Фур'є, спектр.

### **Регулювання напруги – пріоритетний метод підвищення ефективності систем електропостачання харчових виробництв**

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**Вступ.** Підвищити ефективність систем електропостачання підприємств харчової промисловості доцільно шляхом регулювання напруги.

**Матеріали і методи.** Регулювання напруги - ефективний метод підвищення ефективності систем електропостачання. Відхилення напруги є пріоритетним завданням при проектуванні систем електропостачання. Використані математичні апарати теорії ймовірності, математичної статистики й теорії масового обслуговування.

**Результати і обговорення.** Розглянуто шляхи підвищення ефективності харчових виробництв за рахунок зниження технологічних втрат, спричинених неякісною напругою. Запропоновано спосіб підвищення якості напруги. Застосування напівпровідникових приладів дозволяє усунути низку недоліків механічного перемикаючого пристрою (невисоку швидкодію, низький ресурс) і залишити основну його перевагу - синусоїдність форми кривої напруги. Можливість з допомогою напівпровідникових пристроїв здійснювати комутацію без спотворення синусоїди у момент переходу через нуль дозволяє усунути і такий суттєвий недолік механічних перемикачів, як дискретність. Це дає змогу виконати стабілізатори напруги будь-якого ступеня точності, засновані на принципі дискретного регулювання перемиканням відпайок трансформатора без розриву струму та спотворення кривої напруги. Цим пояснюється множина напрямків розробок як у нас, так і за рубежом у напрямку заміни контакторних комутаторів у діючих на сьогодні пристроях РПН на тиристорні.

**Висновки.** Результати дослідження рекомендуємо застосовувати на всіх підприємствах харчової промисловості з метою підвищення ефективності використання електроенергії.

**Ключові слова:** напруга, електроенергія, електрообладнання, збиток.

## Процеси і обладнання харчових виробництв

### Спектральна підмодель випромінювання для 3-D моделювання спалювання метану

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**Вступ.** Наявність адекватної валідної моделі горіння метану дозволить моделювати подібні процеси в промислових пальниках.

**Матеріали та методи.** Моделювання горіння метану в пальниках проведено з використанням програмного забезпечення FLUENT і CFX. Коефіцієнт поглинання, отриманий на основі «сірих» моделей, виправлений з урахуванням частки випромінювання чорного тіла в спектрах трьохатомних газів у продуктах згоряння.

**Результати і обговорення.** Дослідження відноситься до 3-D моделювання процесу «м'якого» спалювання метану і, зокрема, стосується розробки підмоделі визначення радіаційних характеристик продуктів спалювання. Виконаний аналіз радіаційного теплообміну, на основі якого була розроблена підмодель для визначення усередненого лінійного коефіцієнта поглинання. Дана модель, враховуючи середні значення коефіцієнтів поглинання продуктів згоряння, ґрунтується на розрахунку спектральної частки випромінювання компонентами димових газів стосовно випромінювання абсолютно чорного тіла. Розроблено CFX 3-D модель спалювання метану в циліндричному лабораторному пальнику. Модель інкорпорує розроблену підмодель спектрального поглинання. Результати розрахунків, виконані в рамках розробленої CFX 3-D моделі, були зіставлені з наявними в літературі експериментальними даними, отриманими за відповідних режимів і витратних параметрів процесу. Зіставлення демонструє близьку відповідність результатів, що підтверджує адекватність і валідність розробленої оптичної підмоделі для визначення усереднених лінійних коефіцієнтів поглинання продуктів згоряння і можливість застосування даної моделі для практичного 3-D моделювання процесів спалювання.

**Висновок.** Розроблена підмодель, інкорпорована в 3-D модель спалювання метану, рекомендується для використання в інженерній розрахунковій практиці і в 3-D моделюванні процесів спалювання.

**Ключові слова:** *спалювання, пальник, теплообмін, моделювання.*

### Удосконалення процесу сушіння пивної дробини в апаратах з киплячим шаром

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**Вступ.** З метою удосконалення процесу сушіння пивної дробини в апаратах з киплячим шаром і розробленням нових конструкцій доцільно провести моделювання і розрахунок технологічних процесів з використанням програмних засобів комп'ютерного моделювання та експериментальних досліджень.

**Матеріали і методи.** Досліджено процес сушіння пивної дробини в шнековій сушарці киплячого шару. Пивна дробина має густу консистенцію грубо розмеленого



зернового продукту, світло-коричневий колір, солодкуватий смак і солодовий запах, багата на поживні речовини. Моделювання процесу сушіння пивної дробини проводилося на основі методу кінцевих елементів із застосуванням програмного пакета Flow Vision та математико-статистичних методів.

**Результати і обговорення.** Розроблена математична модель надає можливість визначити тиск теплоносія в сушильній камері, що залежить від швидкості теплоносія і конструкції газорозподільного пристрою, та оптимальні режими роботи сушильної установки. Рівномірне нагрівання та висушування продукту у псевдозрідженому стані в будь-якій точці перетину сушильної камери шнекової сушарки досягається за рахунок якісного розподілення теплоносія над газорозподільним пристроєм. Обґрунтовано доцільність визначення критерію Рейнольдса за напівемпіричною інтерполяційною формулою В.Д. Горошко, Л.Г. Розенбаума, О.М. Тодеса, що дозволило зменшити габаритні розміри сушарки. Удосконалено конструкцію шнекової сушарки, а саме: під перфоровану газорозподільну решітку встановлено профіль, який забезпечує направлений рух теплоносія та вирівнює тиск теплоносія по всій довжині сушильної камери.

**Висновки.** Використання результатів досліджень для вибору режимів сушіння на етапі проектування сушильного обладнання дає змогу удосконалити процес сушіння пивної дробини в шнековій сушарці.

**Ключові слова:** пиво, дробина, сушіння, шнек.

### **Моделювання процесу вібраційного сушіння соняшнику при використанні теорії подібності**

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**Вступ.** Мета досліджень - розробити критеріальне рівняння для розрахунку кінетики сушіння насіння соняшника у вібраційній сушарці з U-подібним контейнером.

**Матеріали і методи.** Використані основні положення теорії подібності для тепломасообмінних процесів, динаміки руху віброзрідженого шару сипкої продукції, методи теплофізичного експерименту.

**Результати і обговорення.** Складено критеріальне рівняння в узагальнених змінних процесу сушіння насіння соняшнику. У зв'язку з малим діапазоном вимірюваних величин та, відповідно, великою розбіжністю числа Стантона узагальнені числа Стантона визначено при різних завантаженнях робочого контейнера на основі графіків залежності модифікованого вібраційного числа Стантона від модифікованого вібраційного числа Пекле. Складена залежність дозволяє більш точно врахувати вібраційні ефекти при реалізації тепломасообмінних процесів, зокрема збільшення поверхні тепломасообміну, зменшення коефіцієнта внутрішнього тертя та сухої в'язкості технологічного середовища. Останні чинники створюють сприятливі умови для потенційного зменшення енерговитрат при транспортуванні й тепловій обробці сипкої продукції. Вібраційна технологічна дія залишається основним фактором для регулювання динамічного стану об'єкта обробки, зокрема при погашенні нестабільності системи за рахунок розсіювання енергії у сипкій масі.

**Висновки.** Рівняння рекомендується для розрахунку кінетики сушіння насіння соняшника в діапазоні числа Пекле  $1.3 < Pe < 2$ , для степені завантаження робочого контейнера  $0,33 < \Pi < 0,67$  та при відношенні температур зерна під час сушіння та його початкового значення в межах  $2,2 < T < 3,4$ .

**Ключові слова:** сушіння, вібрація, соняшник, насіння.

### Адсорбційне очищення водно-спиртових розчинів від вищих спиртів шунгітом

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**Вступ.** Мета досліджень - підвищення якості та безпеки водно-спиртових розчинів за рахунок використання природного адсорбенту шунгіту.

**Матеріали і методи.** Досліджуються водно-спиртові розчини концентрацією 40% і природний адсорбент шунгіт. Розчин пропускали через шар шунгіту. Вміст вищих спиртів визначено калориметричним методом. Покомпонентний склад вищих спиртів встановлювали за допомогою хроматографа "Agileut HP-6890", що має колонку HP FFAP 50m/032 mm-mkm.

**Результати і обговорення.** Тривалість взаємодії водно-спиртового розчину та шунгіту 20 хв є оптимальною в процесі очищенні. Вищі спирти ефективніше адсорбуються при температурі розчину 0-10<sup>0</sup>С, зменшуючи свій вміст із 12,5 до 1,5 мг/дм<sup>3</sup>. Підвищення температури водно-спиртового розчину із 10 до 25<sup>0</sup>С супроводжується підвищенням кількості вищих спиртів із 1,5 до 2 мг/дм<sup>3</sup>. Проведення процесу очищення при температурі водно-спиртового розчину вище 25<sup>0</sup>С є недоцільним. Шунгіт ефективно адсорбує шкідливі для здоров'я людини вищі спирти. Вміст н-пропанолу зменшується з 0,41 до 0,14 мг/дм<sup>3</sup>. Аналогічно зменшується вміст і-пропанолу – від 1,71 до 1,35 мг/дм<sup>3</sup>. Вміст метанолу у вихідному водно-спиртовому розчині зменшується з 0,0016 до 0,00035 мг/дм<sup>3</sup>. Це пояснюється тим, що шунгіт має розвинену пористу структуру та високі адсорбційні властивості. Наявність родовищ шунгіту, його невисока вартість та екологічна безпечність обумовлює його використання для очищення водно-спиртових розчинів. Зменшення концентрації вищих спиртів у водно-спиртових розчинах покращує органолептичні властивості алкогольних напоїв і підвищує їхню споживчу якість.

**Висновки.** Результати досліджень рекомендується використовувати для виробництва алкогольних напоїв. Це покращить їхню якість і безпечність.

**Ключові слова:** алкоголь, очищення, шунгіт, адсорбція, спирт.

### Гідродинамічні і дифузійні параметри електроосмотичного зневоложення пектиномісткої сировини

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**Вступ.** При зневоложенні пектиномісткої сировини постає необхідність підвищення ефективності вилучення зв'язаної вологи за умови мінімізації

пошкодження клітинної структури, що можна реалізувати за рахунок електроосмотичного відтискування вологи.

**Матеріали і методи.** Використано аналітичні методи дослідження, що ґрунтуються на сучасних концепціях теорії поверхневого шару, основних положеннях гідродинаміки різних середовищ та електродинаміки руху дифузійної рідини.

**Результати і обговорення.** Електроосмотичне зневоложення сприяє скороченню тривалості сушіння сировини, зниженню втрат біологічно активних речовин. Визначено рівняння сили електроосмотичної дифузії, основні закономірності електроосмотичного кінетичного процесу руху рідкої фази, залежності основних параметрів електрогідродинаміки осмотичного масоперенесення. З урахуванням особливостей пектиномісткої сировини отримано залежність для сили електрокінетичного тиску на дифузійну рідину. За реалізації електроосмотичного зневоложення означеної сировини на експериментально-промисловій моделі технологічної машини як інтенсифікаційні чинників були обрані: вібровідцентрова дія на масу продукції, що дозволяє максимально її ущільнити при пропусканні електричного струму; створення віброзваженого стану продукції на другому етапі обробки, що надає можливість значно збільшити ефективність дії конвективного потоку теплоносія. Такі фактори разом із електроосмотичною складовою істотно підвищують рушійну силу досліджуваного процесу зневоложення.

**Висновки.** Мінімізацію пошкодження структури пектиномісткої сировини при підвищенні поверхні масообміну можна досягнути також за рахунок створення віброзрідженого шару.

**Ключові слова:** *зневоложення, електроосмос, пектин, гідродинаміка.*

## Аннотации

### Пищевые технологии

#### Исследование состава пищевых эмульгаторов ацилглицеринной природы методом инфракрасной спектроскопии

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**Введение.** Исследовано состав пищевых эмульгаторов, полученных из рафинированного подсолнечного масла в мягких условиях с целью определения в них содержания моно- и диацилглицероов жирных кислот и доказательства сохранения эссенциальных биологически активных компонентов, замедления процессов термоокисления.

**Материалы и методы.** Качественное и количественное изучение состава эмульгаторов ацилглицеринной природы, полученных в мягких условиях (35...40 °С), выполнено с использованием инфракрасной спектроскопии на Фурье-спектрометре Perkin-Elmer Spectrum One FTIR Spectrometer методом раздавленной капли.

**Результаты и обсуждение.** Изучено инфракрасные спектры новых эмульгаторов ацилглицеринной природы и выполнен анализ характеристических полос поглощения, отнесенных к соответствующим типам валентных и деформационных колебаний триацилглицеринов ( $1110\text{ см}^{-1}$ ,  $1173\text{ см}^{-1}$ ,  $1244\text{ см}^{-1}$  -  $\nu(\text{C}=\text{O})$  эстеров;  $1377\text{ см}^{-1}$  и  $1416\text{ см}^{-1}$  -  $\delta_s(\text{C}-\text{H})$  в группах  $-\text{CH}_3$  и  $-\text{CH}_2-$ ;  $1736\text{ см}^{-1}$  -  $\nu(\text{C}=\text{O})$  эстеров;  $2855\text{ см}^{-1}$  и  $2927\text{ см}^{-1}$  -  $\nu(\text{C}-\text{H})$  в группах  $-\text{CH}_2-$ ;  $3009\text{ см}^{-1}$  -  $\nu_{as}(\text{C}-\text{H})$  в группах  $-\text{CH}=\text{CH}-$  в *cis*-форме), гидроксильных групп моно- и диацилглицеринов жирных кислот ( $3435\text{ см}^{-1}$ ), первичных спиртов ( $1061\text{ см}^{-1}$ ).

Доказано присутствие в составе новых эмульгаторов моно- и диацилглицеринов жирных кислот и установлено, что благодаря мягким условиям их получения они не содержат трансизомеров и в них сохранены ненасыщенные кислоты в нативной форме.

На основе вычисленных спектральных характеристик (пиковой интенсивности, ширины полосы поглощения, площади  $S$ , ограниченной кривой и горизонтальной нулевой линией) построен градуировочный график зависимости величины  $S$  от массовой доли моно- и диацилглицеринов в модельных композициях E471 с рафинированным подсолнечным маслом. С помощью полученного уравнения прямой определено суммарное содержание моно- и диацилглицеринов жирных карбоновых кислот в новых пищевых эмульгаторах, которое составило  $54,2 \pm 1,2\%$ .

**Выводы.** Предложено использование метода ИК-спектроскопии для решения задач количественного определения моно- и диацилглицеринов жирных кислот в эмульгаторах ряда ацилглицеринов E471.

**Ключевые слова:** эмульгатор, ацилглицерин, моноацилглицерин, спектроскопия, поглощение.

## **Изменения каротина в процессе получения пищевых добавок на основе моркови**

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**Введение.** Цель исследований - разработка новых технологических решений для более полного использования полезных свойств моркови для получения двух каротинсодержащих полифункциональных пищевых добавок в сухом и жидком виде.

**Материалы и методы.** Использовались корнеплоды моркови сорта Шантане 2461, морковный сок, выжимки, порошкообразный каротинсодержащий обогатитель с морковных выжимок, жидкий концентрированный каротинсодержащий наполнитель из морковного сока и продукция комплексной переработки моркови. Химический состав всех образцов определяли согласно международным стандартам.

**Результаты и обсуждение.** В работе предложена комплексная ресурсосберегающая технология переработки моркови с получением двух базовых каротиносодержащих продуктов-сухого и жидкого. Сухой обогатитель "Каротинка", полученный в производственных условиях путем СВЧ-сушки морковных выжимок, отличается высоким содержанием  $\beta$ -каротина (148,0-154,0 мг/100 г) и клетчатки (11 г/100 г). Жидкий наполнитель "Морковный мед", полученный на основе морковного сока (70% сухих веществ), богатый на сахара (52-55 г/100 г),  $\beta$ -каротин (до 11-12 мг/100 г) и пектиновые вещества (до 4 г/100 г).

Полученные продукты подвергали различным технологическим воздействиям. Можно отметить сравнительно высокую устойчивость полученных пищевых добавок к различным режимам технологического процесса.

Апробирован ряд технологий по получению консервированных продуктов с использованием наполнителя "Морковный мед", а также разработаны новые рецептуры кондитерских и хлебобулочных изделий.

**Выводы.** Полученные каротинсодержащие продукты можно использовать в пищевых технологиях в качестве полифункциональных обогащающих добавок.

**Ключевые слова:** *морковь, каротин, сушка, концентрирование, добавка.*

## **Анализ спектров диффузного отражения сухого молока и их связь с технологическими параметрами**

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**Введение.** С целью усовершенствования продуктов для детского питания проведены исследования состава сухого молока животных. Изучение спектров диффузного отражения различных пищевых продуктов дает возможность определять различные физико-химические показатели.

**Материалы и методы.** Инфракрасные спектры отражения сухого молока, которое предлагается использовать в детском питании, были исследованы с помощью прибора «Инфрапид-61». Спектры диффузного отражения сухих молочных продуктов изучались в диапазоне 1330-2370 нм с шагом в 10 нм.

**Результаты и обсуждение.** Спектры диффузного отражения сухого молока таких домашних животных, как козы, кобылы и овцы несколько схожи, но на определенных длинах волн существуют и значительные различия. Все исследуемые спектры отражения кобыльего и козьего сухого молока подобные по своей форме. Спектр отражения овечьего сухого молока несколько отличается от предыдущих. На длине волны 1720 нм для всех трех спектров наблюдается минимум отражения, но в спектре кобыльего молока этот экстремум заметно меньше. Аналогичные выводы можно сделать, анализируя спектры на длинах волн 2310 и 2350 нм. К особенностям следует отнести и то, что в интервале длин волн 2010-2220 нм спектр отражения кобыльего сухого молока представляет собой монотонную кривую с одним экстремумом на длине волны 2110 нм. В то же время в спектрах отражения овечьего и козьего сухого молока проявляются по два экстремума на длинах волн 2060 и 2170 нм соответственно.

Важным спектральным диапазоном является интервал длин волн 1480-1500 нм, который отвечает за наличие белков в образцах. Особенно глубокий минимум характерен для кобыльего молока, которое в своем химическом составе имеет наименьшее количество белков, что подтверждается независимыми опытами. Содержание белка в козьем и овечьем сухом молоке существенно не отличается. Это качественно подтверждают, результаты анализов спектров отражения.

**Выводы.** Проведенные исследования диффузных спектров отражения в ближнем инфракрасном диапазоне обнаружили существенные различия в спектральном распределении для козьего, овечьего и кобыльего сухого молока и дали возможность проводить качественный анализ.

**Ключевые слова:** *молоко, спектроскопия, спектр, анализ.*

### **Кисломолочный напиток с антиоксидантными свойствами**

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**Введение.** Использование пектина и Р-витаминного комплекса, выделенного из зеленого чая, в качестве функциональных ингредиентов кисломолочных напитков позволит расширить ассортимент, улучшить консистенцию готового продукта, а также повысить его пищевую ценность.

**Материалы и методы.** Оценку вкуса и запаха кисломолочного напитка проводили с использованием профильного метода, основанного на том, что отдельные импульсы вкуса и запаха, объединяясь, дают качественно новый импульс совместной вкусовой и душистой характеристики продукта. Исследование структурно-механических свойств исследуемых образцов проводили на вискозиметре типа «Реотест-2». Органолептические показатели напитков оценивали с использованием пятибалльной шкалы для оценки выраженности соответствующего образца.

**Результаты и обсуждение.** Наиболее оптимальный профиль по всем рассматриваемым дискреторам получил образец кисломолочного напитка с цитрусовым пектином, который характеризуется как гармоничный, кисломолочный, освежающий, с выраженным цитрусовым запахом.

На основании исследований образцов кисломолочного напитка установлено, что они относятся к коагуляционным структурам. Проведенный анализ рассчитанных реологических параметров показал, что исследуемые образцы с пектином и Р-витаминным комплексом относятся к структурированному твердоподобному телу, имеют наибольшую прочность структурированных связей, им свойственна тиксотропия. Наиболее прочный структурированный каркас наблюдается в исследуемом образце с содержанием фруктового пектина и Р-витаминного комплекса, а также с содержанием цитрусового пектина.

**Выводы.** При использовании фруктового пектина с Р-витаминным комплексом значительно улучшается консистенция и структура кисломолочного продукта, а также лучше проявляются дискрепторы вкуса и запаха.

**Ключевые слова:** *молоко, пектин, витамин Р.*

### **Применение полимеров в качестве носителей для инкапсуляции олеорезинов специй**

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**Введение.** Обобщена информация по олеорезинам специй, различным полимерам для их инкапсуляции и исследованы системы носителей на основе мальтодекстрина и диоксида кремния.

**Материалы и методы.** Материалом исследований были инкапсулированные формы олеорезина розмарина и черного перца, инкапсулированные смесью мальтодекстрина и диоксида кремния. Изучали влияния концентрации олеорезина в колбасных изделиях на изменение их сенсорных показателей и стабильность микрофлоры вареных колбас по стандартным методикам.

**Результаты и обсуждение.** Представлен обзор возможных носителей для олеорезинов. Описаны последние результаты испытаний по носителям, таким как углеводы, крахмалы, мальтодекстрины, камеди, протеины. Особое внимание уделяется преимуществам и недостаткам каждой системы инкапсуляции. Показывается и анализируется влияние различных комбинаций покрывающих материалов на эффективность инкапсуляции. Описывается исследование системы носителей на основе мальтодекстрина и диоксида кремния для инкапсулирования олеорезинов черного перца и розмарина. Приведены данные о бактериостатическом воздействии инкапсулированных форм олеорезинов перца черного и розмарина.

Получен комплекс "гость-хазяин" олеорезина черного перца, инкапсулированного в смеси мальтодекстрина (ДЕ15-20) и диоксида кремния (А300) в соотношении 95:5. Срок хранения вареных колбас был увеличен вдвое в случае использования этого комплекса "гость-хазяин" в концентрации 0,2%. Содержание черного перца в вареных колбасах составило 0,042%, что не превышает максимально установленный уровень.

**Выводы.** Инкапсулированная форма олеорезина черного перца, а также его комбинирование с инкапсулированной формой олеорезина розмарина в процессе хранения стабилизируют значение микрофлоры лучше, чем инкапсулированная форма олеорезина розмарина, даже при увеличении доли растительного наполнителя и влаги на основное сырье.

**Ключевые слова:** *чёрный перец, розмарин, колбаса, олеорезин, инкапсуляция.*

## Установление равновесного состояния водок с помощью $^1\text{H}$ ЯМР спектроскопии

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им. Михаила Туган-Барановского, Донецк, Украина

**Введение.** Цель исследований - выявление равновесного состояния гидроксильных протонов этанола и воды в водках и водках особых, произведенных в Украине, с помощью  $^1\text{H}$  ЯМР спектроскопии.

**Материалы и методы.** С помощью мерной пипетки задавали необходимый объем (0,3 мл) водки или водки особой. Необходимый для работы системы LOCK'a - дейтериевой стабилизации ЯМР спектрометра ацетон- $\text{d}_6$  - внешний стандарт, который отделен от исследуемого вещества, вносили в ампулу в капилляре специальной формы, запись спектров  $^1\text{H}$  ЯМР и обработку данных проводили в соответствии с инструкцией, которая прилагается к Фурье ЯМР спектрометру Bruker Avance II (400 MHz).

**Результаты и обсуждение.** Экспериментально определены элементы установления термодинамического равновесия гидроксильных протонов этанола и воды в водках и водках особых с помощью  $^1\text{H}$  ЯМР спектроскопии. Выделены 3 группы образцов исходя из равновесия гидроксильных групп протонов воды и этанола: неустановившегося, переходного, установившегося равновесия. Установившееся равновесие характеризуется наличием в гидроксильной группе объединенного унитарного сигнала  $\text{EtOH}+\text{H}_2\text{O}$  ( $\delta_{\text{EtOH}+\text{H}_2\text{O}}=4,75\dots 4,80$  ppm). Неустановившееся и переходное равновесие характеризуются наличием в гидроксильной группе двух отдельных сигналов  $\text{EtOH}$  ( $\delta_{\text{EtOH}}=5,34$  ppm) и  $\text{H}_2\text{O}$  ( $\delta_{\text{H}_2\text{O}}=4,72\dots 4,75$  ppm). Отличительной их особенностью является то, что неустановившееся равновесие характеризуется явным присутствием гидроксильного протона этанола ( $\text{EtOH}$ ), а переходное - наличием едва заметного сигнала  $\text{EtOH}$ , который характеризует переход от установившегося к неустановившемуся равновесию.

**Выводы.** Существует принципиальное отличие поведения гидроксильных протонов этанола и воды в водках и водках особых. Полученные равновесные системы позволяют усовершенствовать технологический процесс производства водки на ликеро-водочных предприятиях для стабилизации качества готовой продукции.

**Ключевые слова:** водка, равновесие, гидроксил, протон, спектроскопия.

## Влияние соотношения водной и масляной фазы эмульсий с крахмалом на вязкость, плотность, размер частиц и мутность системы

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**Введение.** Необходимо определить оптимальное соотношение водной и масляной фаз, режима смешивания двух фаз, выбор параметров гомогенизации, в которых получается устойчивая эмульсионная система.

**Материалы и методы.** Для исследований готовились 5 образцов пищевых эмульсий с переменным количеством масляной фазы и постоянным количеством стабилизатора (крахмала) и 5 образцов пищевых эмульсий с использованием разного количества крахмала при постоянном количестве масляной фазы. Вязкость эмульсий определена на вискозиметре Brookfield, размер частиц - на микроскопе Eastcolight



92012-ES (100x, 250x, 550x, 750h), мутность - на мутномере 2100b, плотность - на лабораторном ареометре.

**Результаты и обсуждение.** Анализ эмульсий с переменным количеством масляной фазы и постоянным количеством крахмала показывает, что чем больше показатель масляной фазы, тем выше вязкость, мутность, плотность, pH и размер частиц эмульсии, но размер частиц не должен превышать 1 мкм. Анализ эмульсий с использованием разного количества крахмала при постоянном количестве масляной фазы показывает, что чем больше крахмала в составе продукта, тем меньше размер частиц эмульсии, мутность, что улучшает стабильность эмульсионной системы. Увеличение количества стабилизатора улучшает стабильность эмульсии, так как уменьшается размер частиц, но мало влияет на мутность. При недостаточном количестве стабилизатора образуются частицы размером более 1 мкм, что может привести к появлению «жирового кольца» в системе при хранении. Лучший результат исследования эмульсий с крахмалом состоит в том, что бы это получить максимальное количество частиц около 1 мкм.

**Выводы.** Результаты могут служить основой для создания технологии производства эмульсий как класса пищевых продуктов и новых пищевых продуктов.

**Ключевые слова:** *крахмал, эмульсия, гомогенизация.*

#### **Аномальные свойства в водных растворах полисахаридов**

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**Введение.** Исследование физико-химических свойств суспензий полисахаридов в широком интервале механических напряжений и температур важно при обосновании технологических режимов производства пищевых продуктов.

**Материалы и методы.** Готовили 0,5 % суспензии гуаровой, ксантановой камеди и камеди рожкового дерева, 1,5% суспензию пектина и 10 % суспензию нативного картофельного крахмала в дистиллированной воде. Все суспензии термостатировали в течение 30 мин при различных температурах в диапазоне 20-90<sup>0</sup>С.

**Результаты и обсуждение.** Существование на дифрактограммах исследуемых полисахаридов широкой полосы свидетельствует о том, что при их растворении в воде существуют или образуются ассоциаты молекул полимера и воды. Анализ микрофотографий образцов полисахаридов подтверждает это. Кристалличность ассоциатов камедей проявляется довольно слабо, что может быть связано с отличной от крахмалов структурой самих молекул камедей с разветвленными боковыми цепями. С повышением температуры водных растворов полисахаридов выше 40<sup>0</sup> С разрушается квазикристаллическая структура комплексов молекул, растет подвижность молекул раствора, в результате чего возникает более неупорядоченная структура. При этом должна увеличиваться плотность раствора, которая вызывает повышение его вязкости до температуры 40<sup>0</sup> С, выше которой вязкость начинает уменьшаться. Такое аномальное поведение растворов можно объяснить полиморфными превращениями в диапазоне температур 35-55<sup>0</sup> С самих молекул полисахаридов при увеличении свободы движений, что подтверждается существованием экзотермического пика на кривых дифференциальной сканирующей калориметрии.

**Вывод.** В результате полиморфных преобразований увеличивается активность молекул полисахаридов в межмолекулярных взаимодействиях.

**Ключевые слова:** *полисахарид, крахмалл, квазикристалл, суспензия.*

**Влияние частичного гидролиза на экстрагирование белков  
из подсолнечного шрота**

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**Введение.** Исследовано влияние степени гидролиза белков в присутствии нейтральной протеазы *Bacillus subtilis* на процесс экстрагирования белков из подсолнечного шрота. Проанализирована корреляция между степенью гидролиза белков и эффективностью их экстрагирования.

**Материалы и методы.** Степень гидролиза белков определяли как увеличение концентрации белков, растворимых в трихлоруксусной кислоте, в сравнении из контрольными образцами. Концентрацию белков в экстрактах определяли фотометрическим методом.

**Результаты и обсуждение.** Определение концентрации белков в полученных экстрактах показало, что главная часть белков экстрагировалась в течение первых 20 минут. Концентрация белков в экстрактах, полученных с использованием протеазы, была примерно в два раза выше в сравнении из контрольными образцами. При низком соотношении фермент:субстрат степень гидролиза белков была достаточно низкой – в пределах от 3,5 % до 5,2 %. При увеличении соотношения фермент:субстрат степень гидролиза увеличивалась и достигала 9,0-9,5 % в течение 40-60 минут. Такой уровень гидролиза белков может приводить к усовершенствованию функциональных свойств белков, в то время как более высокий уровень гидролиза вызывает потерю функциональности белков. Таким образом, степень гидролиза белков зависела от соотношения фермент:субстрат и от длительности реакции.

Получена нелинейная модель оценки эффективности экстрагирования белков как функции от соотношения фермент:субстрат и от длительности. Такая модель охватывает 92,81% полученных экспериментальных данных и хорошо аппроксимирует полученные результаты. Существует достаточно высокая корреляция между концентрацией белков в экстрактах степенью гидролиза белков.

**Выводы.** Частичный гидролиз белков подсолнечного шрота под воздействием нейтральной протеазы увеличивал концентрацию белков в экстрактах. Полученная модель может быть использована для прогнозирования степени гидролиза белков при экстрагировании их в присутствии протеолитических ферментов а также их функциональных свойств.

**Ключевые слова:** *подсолнечник, гидролиз, белок, протеаза, гидролизата.*

**Обогащение пищевых продуктов эссенциальными микроэлементами и  
безопасность жизни человека: обзор литературы**

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**Введение.** Детальное исследование взаимодействий микроэлементов (Mn, Fe, Cu, Se, Zn, I и др.) в организме человека позволяет решить ряд проблем, связанных с предупреждением и лечением болезней, вызванных дисбалансом микроэлементов.

**Материалы и методы.** Проанализирована современная литература о принципах обогащения пищевых продуктов микроэлементами. Рассматривались такие вопросы, как острая токсичность, значение, биологическая роль и расстройства, вызванные недостатком этих микроэлементов.

**Результаты и обсуждение.** Обогащение микроэлементами необходимо тщательно контролировать, принимая во внимание токсический эффект, вызываемый повышенной концентрацией этих элементов. Считается, что рост потребления Zn с 5 до 20 мг в день в рационе питания человека необходимо компенсировать увеличением в 16 раз употребление Cu с целью сохранения баланса. Согласно экспериментальным исследованиям, рост концентрации каждого из этих микроэлементов приводит к уменьшению биодоступности каждого из них. Одновременное усвоения эссенциальных микроэлементов может углублять конкуренцию между ними, начиная с кишечника и заканчивая специфическими взаимодействиями с белками, лигандами и тому подобное. Взаимодействие между микроэлементами может быть как синергическим, так и антагоническим.

**Выводы.** Наиболее важными микроэлементами для организма человека и, соответственно, для обогащения пищевых продуктов являются Fe, Zn, I и Se, в частности хлебопекарских.

**Ключевые слова:** *микроэлемент, цинк, обогащение, дефицит, токсичность.*

## Биотехнология, микробиология

### Влияние апипродуктов на структурно-механические и физико-химические свойства йогурта

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**Введение.** Предложено повысить биологическую и пробиотическую ценность йогурта добавлением продуктов пчеловодства. Определено влияние этих продуктов на потребительские свойства йогурта.

**Материалы и методы.** Используемые материалы: нормализованное молоко, сухие бактериальные закваски сублимационной сушки, мед акации, маточное молочко, пыльца. Отбор, подготовка и испытания проводились с помощью стандартных методов анализа. Реологические параметры были определены с использованием ротационного вискозиметра. Степень синерезиса была определена путем фильтрации, влагоудерживающая способность – путем центрифугирования. Для определения относительной вязкости использовали вискозиметр течения.

**Результаты и обсуждение.** Изучение эффективной вязкости образцов показало, что добавление в йогурт меда в количестве 5% увеличивает эффективную вязкость при незначительном разрушения сгустка на  $28 \pm 1\%$  и уменьшает – при существенном разрушения на  $72,5 \pm 2, 5\%$ . Образцы с медом и маточным молочком разрушались быстрее и имели высокий индекс текучести – 0,451, но их тиксотропная способность была выше, чем в контрольной группе. Внесение в йогурт комплексной добавки меда, маточного молочка и пыльцы стабилизирует вязкость и ускоряет восстановление его структуры после разрушения. Это поможет улучшить консистенцию после разлива при резервуарном способе производства.

Наименьшая устойчивость к влагоотдачи была у образцов со смесью меда и маточного молочка – синерезис = 42мл, ВУЗ = 52%. Высокая - с 5% меда (39мл), и ВУЗ – 55% соответственно. Образец содержащий 5% меда, 0,2% маточного молочка и 0,2% пыльцы, имел не самые лучшие синеретические свойства среди опытных проб йогурта, но по всем показателям превышал контрольный. Титруемая кислотность в образцах йогурта с медом в течение девяти дней нарастала быстрее, чем у других исследуемых образцов. На шестые сутки хранения она составила более 150 °Т, что выше допустимой нормы на 10°Т.

**Выводы.** Наилучшими показателями владел йогурт, имевший в своем составе комбинированную добавку с апипродуктов (мед, маточное молочко, пыльца - 5%, 0,2 и 0,15%, соответственно).

**Ключевые слова:** мед, пчеловодство, йогурт.

## Автоматизация технологических процессов

### Алгоритмы быстрого преобразования Фурье в задачах спектральной обработки сигналов в системах реального времени

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**Введение.** Рассмотрены алгоритмы реализации быстрого преобразования Фурье (БПФ) в системах цифровой фильтрации сигналов, позволяющие сократить объем вычислений и время обработки "скользящей" последовательности дискретных колебаний.

**Методы.** Использован единый матричный подход к алгоритмам быстрого дискретного преобразования Фурье.

**Результаты и обсуждение.** Дискретное преобразование Фурье конечной последовательности отсчетов представляется в комплексной матричной форме, что позволяет определить структуру полного распараллеливания процесса спектральной обработки по принципу разреживания по времени или разреживания по частоте для "скользящей" последовательности дискретных колебаний. Разработаны алгоритмы, позволяющие реализовать операцию "скользящего" спектрального анализа с максимальным использованием цифровой информации о спектре для предыдущего положения "временного окна". Кроме того, при матричном подходе в самом алгоритме заложены основные группирующие фрагменты для эффективного распараллеливания вычислительного процесса спектральной обработки по принципу разреживания по времени или разреживания по частоте, в том числе для "скользящей" последовательности дискретных колебаний. В качестве примера рассчитаны значения «поворачивающих множителей» для дискретного Фурье – преобразования последовательности 16 отсчетов радиолокационного сигнала с «шагом скольжения»  $\Delta N=4$ . Для 16 отсчетов следующего «временного окна» согласно схеме 12 из 16 значений на выходе модуля обработки не пересчитываются (2-4 строки по 4 элемента первого «окна» становятся 1-3 строками второго окна, 2-4 строки второго «окна» становятся 1-3 строками третьего «окна» и т. д.), и только 4 из 16 нужно вычислять на каждом шаге «скольжения».

**Выводы.** Предложенные алгоритмы существенно сокращают объем вычислений и могут быть использованы, например, в автоматизированных системах обработки радиолокационных сигналов, работающих в реальном времени.

**Ключевые слова:** *алгоритм, радиолокация, быстрое преобразование Фурье, спектр.*

### **Регулирование напряжения – приоритетный метод повышения эффективности систем электроснабжения пищевых производств**

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**Введение.** Повысить эффективность систем электроснабжения предприятий пищевой промышленности рекомендуется путем регулирования напряжения.

**Материалы и методы.** Регулирование напряжения - эффективный метод повышения эффективности систем электроснабжения. Отклонение напряжения - приоритетное задание при проектировании систем электроснабжения. Используются математические аппараты теории вероятности, математической статистики и теории массового обслуживания.

**Результаты и обсуждение.** Рассмотрены пути повышения эффективности пищевых производств путем снижения технологических потерь, вызванных некачественным напряжением. Предложен способ повышения качества напряжения. Использование полупроводниковых приборов позволяет исключить ряд недостатков механических переключающих устройств (инерционность, низкий ресурс работы) и оставить основное его преимущество – синусоидальность формы кривой напряжения. Возможность с помощью полупроводниковых устройств производить коммутацию без искажения синусоиды в момент перехода через нуль позволяет исключить и такой важный недостаток механических переключателей, как дискретность. Это позволяет создать стабилизаторы напряжения высокой точности на принципе дискретного регулирования переключением отпаек трансформатора без разрыва тока и искажения кривой напряжения. Этим объясняется множество направлений разработок как у нас, так и за рубежом в направлении замены контакторных коммутаторов в действующих сегодня устройствах РПН на тиристорные.

**Выводы.** Результаты исследования рекомендуем использовать на всех предприятиях пищевой промышленности с целью повышения эффективности использования электроэнергии.

**Ключевые слова:** *напряжение, электрооборудование, ущерб, электроэнергия.*

## Процессы и оборудование пищевых производств

### Спектральная подмодель излучения для 3-D моделирования сжигания метана

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**Введение.** Наличие адекватной валидной модели сжигания метана позволит моделировать подобные процессы в промышленных горелках.

**Материалы и методы.** Моделирование горения метана в горелках проведено с использованием программного обеспечения FLUENT и CFX. Коэффициент поглощения, полученный на основе "серых" моделей, исправлен с учетом части излучения черного тела в спектрах трёхатомных газов в продуктах сгорания.

**Результаты и обсуждение.** Работа относится к 3-D моделированию процесса "мягкого" сжигания метана, и, в частности, разработке подмодели определения радиационных характеристик продуктов сгорания. Выполнен анализ радиационного теплообмена, на основе которого разработана подмодель для определения усредненного линейного коэффициента поглощения. Данная модель, учитывая средние значения коэффициентов поглощения продуктов сгорания, основывается на расчете спектральной части излучения компонентами дымовых газов по отношению к излучению абсолютно черного тела. Была разработана CFX 3-D модель сжигания метана в цилиндрической лабораторной горелке. Модель инкорпорирует разработанную подмодель спектрального поглощения. Результаты расчетов, выполненные в рамках разработанной CFX 3-D модели, сопоставлены с имеющимися в литературе экспериментальными данными, полученными при соответствующих режимах и расходных параметрах процесса. Сопоставление демонстрирует близкое соответствие результатов, которое подтверждает адекватность и валидность разработанной оптической подмодели для определения усредненных линейных коэффициентов поглощения продуктов сгорания и возможность применения данной модели для практического 3-D моделирования процессов сгорания.

**Вывод.** Разработанная подмодель, будучи инкорпорированной в 3-D модель сжигания метана, рекомендуется для использования в инженерной расчетной практике и в 3-D моделировании процессов сгорания.

**Ключевые слова:** *сжигание, горелка, теплообмен, моделирование.*

### Усовершенствование процесса сушки пивной дробины в аппаратах с кипящим слоем

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**Введение.** С целью усовершенствования процесса сушки пивной дробины в аппаратах с кипящим слоем и разработкой новых конструкций целесообразно провести моделирование и расчет технологических процессов в них с использованием программных средств компьютерного моделирования и экспериментальных исследований.

**Материалы и методы.** Исследуется процесс сушки пивной дробины в шнековой сушилке кипящего слоя. Пивная дробина имеет густую консистенцию грубо размолотого зернового продукта, светло-коричневый цвет, сладковатый вкус и солодовый запах, богатая питательными веществами.

Моделирование процесса сушки пивной дробины проводилось на основе метода конечных элементов с применением программного пакета Flow Vision и математико-статистических методов.

**Результаты и обсуждение.** Разработанная математическая модель позволяет определить давление теплоносителя в сушильной камере, которое зависит от скорости теплоносителя и конструкции газораспределительного устройства, и оптимальные режимы работы сушильной установки. Равномерный нагрев и высушивание продукта в псевдооживленном состоянии в любой точке пересечения сушильной камеры шнековой сушилки достигается за счет качественного распределения теплоносителя над газораспределительным устройством. Обоснована целесообразность определения критерия Рейнольдса по полумпирической интерполяционной формуле В.Д. Горошко, Л.Г. Розенбаума, О.М. Тодеса, что позволило уменьшить габаритные размеры сушилки. Усовершенствована конструкция шнековой сушилки, а именно: под перфорированную газораспределительную решетку установлен профиль, который обеспечивает направленное движение теплоносителя и выравнивает давление теплоносителя по всей длине сушильной камеры.

**Выводы.** Использование результатов исследований для выбора режимов сушки на этапе проектирования сушильного оборудования позволяет усовершенствовать процесс сушки пивной дробины в шнековой сушилке.

**Ключевые слова:** пиво, дробина, сушка, шнек.

### **Моделирование процесса вибрационной сушки подсолнуха при использовании теории подобия**

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**Введение.** Цель исследований - разработать критериальное уравнение для расчета кинетики сушки семян подсолнуха в вибрационной сушилке из U-образным контейнером.

**Материалы и методы.** Используются основные положения теории подобия для тепломассообменных процессов, динамики движения виброоживленного слоя сыпучей продукции, методы теплофизического эксперимента.

**Результаты и обсуждение.** Составлено критериальное уравнение в обобщенных переменных процесса сушки семян подсолнуха. В связи с малым диапазоном измеряемых величин и, соответственно, большим расхождением числа Стантона определяем обобщенные числа Стантона при разных загрузках рабочего контейнера, построив графики зависимости модифицированного вибрационного числа Стантона от модифицированного вибрационного числа Пекле. Составленная зависимость позволяет более точно учесть вибрационные эффекты при реализации тепломассообменных процессов, в частности увеличение поверхности тепломассообмена, уменьшения коэффициента внутреннего трения и, соответственно, сухой вязкости технологической среды. Последние факторы создают благоприятные условия для потенциального уменьшения энергозатрат при транспортировке и тепловой обработке сыпучей продукции. Вибрационное технологическое действие остается основным фактором для регуляции

динамического состояния объекта обработки, в частности при погашении нестабильности системы за счет рассеивания энергии в сыпучей массе.

**Выводы.** Уравнение рекомендуется для расчета кинетики сушки семян подсолнуха в диапазоне числа пекле  $1,3 < Re < 2$ , для степени загрузки рабочего контейнера  $0,33 < П < 0,67$  и при отношении температур зерна во время сушки и его начального значения в пределах  $2,2 < T < 3,4$ .

**Ключевые слова:** сушка, вибрация, подсолнух, семена.

### **Адсорбционная очистка водно-спиртовых растворов от высших спиртов шунгитом**

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**Введение.** Цель исследований - повышение качества и безопасности водно-спиртовых растворов за счет использования природного адсорбента шунгита.

**Материалы и методы.** Исследуются водно-спиртовые растворы концентрацией 40% и природный адсорбент шунгит. Раствор пропускали через слой шунгита. Содержание высших спиртов определены калориметрическим методом. Покомпонентный состав высших спиртов устанавливали с помощью хроматографа "Agileut HP-6890", имеющего колонку HP FFAP 50m / 032 mm-mkm.

**Результаты и обсуждение.** Продолжительность взаимодействия водно-спиртового раствора и шунгита 20 мин является оптимальной в процессе очистке. Высшие спирты эффективно адсорбируются при температуре раствора 0-10 °С уменьшаясь с 12,5 до 1,5 мг / дм<sup>3</sup>. Повышение температуры водно-спиртового раствора с 10 до 25°С сопровождается повышением количества высших спиртов с 1,5 до 2 мг / дм<sup>3</sup>. Проведение процесса очистки при температуре водно-спиртового раствора выше 25°С нецелесообразно. Шунгит эффективно адсорбирует вредные для здоровья человека высшие спирты. Содержание n-пропанола уменьшается с 0,41 до 0,14 мг / дм<sup>3</sup>. Аналогично уменьшается содержание и-пропанола с 1,71 до 1,35 мг/дм<sup>3</sup>. Содержание метанола в исходном водно-спиртовом растворе уменьшается с 0,0016 до 0,00035 мг/дм<sup>3</sup>. Это объясняется тем, что шунгит имеет развитую пористую структуру и высокие адсорбционные свойства. Наличие месторождений шунгита, его невысокая стоимость и экологическая безопасность обуславливают его использование для очистки водно-спиртовых растворов. Уменьшение концентрации высших спиртов в водно-спиртовых растворах улучшает органолептические свойства алкогольных напитков и повышает их потребительское качество.

**Выводы.** Результаты исследований рекомендуется использовать для производства алкогольных напитков. Это улучшит их качество и безопасность.

**Ключевые слова:** алкоголь, очистка, шунгит, адсорбция, спирт.

### **Гидродинамические и диффузионные параметры электроосмотического обезвлаживания пектиносодержащего сырья**

Игорь Паламарчук, Оксана Зозуляк, Владислав Паламарчук  
*Винницкий национальный аграрный университет, Винница, Украина*



**Введение.** При обезвреживании пектиносодержащего сырья возникает необходимость повышения эффективности исключения связанной влаги при условии минимизации повреждения клеточной структуры, что можно реализовать за счет электроосмотического отжимания влаги.

**Материалы и методы.** Используются аналитические методы исследования, которые основываются на современных концепциях теории поверхностного слоя, основных положениях гидродинамики разных сред и электродинамики движения диффузионной жидкости.

**Результаты и обсуждение.** Электроосмотическое обезвреживание способствует сокращению длительности сушки сырья, снижению потерь биологически активных веществ. Определены уравнения силы электроосмотической диффузии, основные закономерности электроосмотического кинетического процесса движения жидкой фазы, зависимости основных параметров электрогидродинамики осмотического массопереноса. Учитывая особенности пектиносодержащего сырья, была получена зависимость для силы электрокинетического давления на диффузионную жидкость. При реализации электроосмотического обезвреживания отмеченного сырья на экспериментально-промышленной модели технологической машины в качестве интенсифицирующих факторов были избраны: виброцентробежное действие на массу продукции, что позволяет максимально уплотнить ее при пропускании электрического тока; создание вибровзвешенного состояния продукции на втором этапе обработки, которая дает возможность значительно увеличить эффективность действия конвективного потока теплоносителя. Такие факторы вместе с электроосмотической составляющей существенно повышают движущую силу исследуемого процесса обезвреживания

**Вывод.** Минимизацию повреждения структуры пектиносодержащего сырья при повышении поверхности массообмена можно достичь за счет создания виброоживленного слоя.

**Ключевые слова:** обезвреживание, электроосмос, пектин, гидродинамика.

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**Автори (рік видання), Назва статті, Назва журналу (курсивом), том (номер), сторінки.**

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 mikrobnnykh poverkhnevo-aktyvnykh rehovyn u biolohii ta medytsyni, *Biotekhnolohiia*, 4(2), pp. 24-38.

*За бажання після транслітерованої назви статті або журналу в {фігурних дужках можна дати переклад англійською мовою}.*

### Посилання на книгу

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#### 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. Donchenko L.V. (2000), *Tekhnologiya pektina i pektinoproduktov*, Deli, Moscow
2. Kirianova H.A. (2008), *Udoskonalennia tekhnolohii termostabilnykh zheleinykh nachynok shliakhom ratsionalnoho vykorystannia hidrokoloidiv roslynnoho ta mikrobnogo pokhodzhennia*: PhD tethis, NUHT, Kyiv.
3. Zalutskiy I.R., Tsybaliuk V.M., Shevchenko C. H. (2009), *Planuvannia i diahnostyka diialnosti pidpriemstva*, Novyi svit, Lviv.

*За бажання після транслітерованої назви книги в {фігурних дужках можна дати переклад англійською мовою}.*

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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](http://www1.nas.gov.ua/publications/q_a/Pages/scopus.aspx)

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