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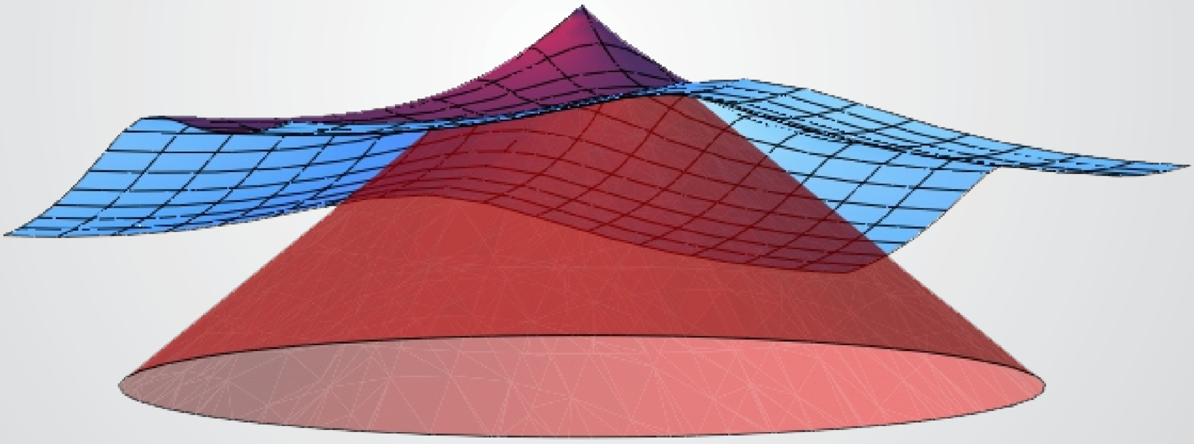

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Web-site: http://mahvp.uft-plovdiv.bg/

Address: 26, Maritza blvd., 4002, Plovdiv, BULGARIA

Phone: +359 32 603 814
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E-mail: mahvp@mail.bg
mahvpuht@gmail.com

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OXIDATIVE STORAGE STABILITY OF COLD PRESSED WALNUT OIL

C. Popovici[*], **O. Deseatnicova**

Faculty of Technology and Management in Food Industry, Technical University of Moldova,
168, Stefan cel Mare Street, MD 2004 - Chisinau, Moldova,
[*]*corresponding author: e-mail*: popovici.kristina@gmail.com

Abstract. *The aim of the work was to evaluate the influence of storage time on quality indices related to walnut oil oxidative stability. Oxidative storage stability was assessed by measuring the primary and secondary oxidation products in cold pressed walnut oil samples immediately after pressing up to 30 weeks of storage. Primary oxidation products of walnut oil samples were evaluated by measuring peroxide value (PV) and conjugated dienes content (CD). Secondary oxidation products of walnut oil samples were evaluated by measuring p-anisidine value (p-AV) and 2-thiobarbituric acid value (2-TBA). Besides, the walnut oil has been chemically characterized using UV/Vis spectra. This method allowed the determination of the main compounds present in walnut oil. Obtained data should help to describe oxidation mechanism of cold pressed walnut oil. However it is necessary to note that these data are not enough to make a final conclusion about the behavior of walnut oil during storage time.*

Key Words: walnut oil, primary and secondary oxidation products, storage stability, shelf life.

I. Introduction

The cold-pressing procedure involves neither heat nor chemical treatments, and it is becoming an interesting substitute for conventional practices because of consumers' desire for natural and safe food products. The consumption of new and improved products such as cold-pressed oils may improve human health and may prevent certain diseases [15].

Over the last few years, increased interest in cold-pressed plant oils has been observed as these oils have better nutritive properties than those after refining. Cold pressing is simple, ecological and does not require much energy. The disadvantage of this process is low productivity and difficulties in obtaining a product of constant quality [15]. Such factors as geographical location, species and processing technique may influence the final chemical composition of plant oils [5, 15].

Walnut kernel (*Juglans regia* L.) is highly appreciated nut because of its unique organoleptic characteristics, biological and nutritional value. Walnuts generally contain about 60% oil, but this can vary from 52 to 70% depending on the cultivar, location grown, and irrigation rate [11]. The major constituents of the oil are triacylglycerols; free fatty acids, diacylglycerols, monoacylglycerols, sterols, sterol esters, and phosphatides are all present in only minor quantities. The major fatty acids found in walnut oil are oleic (18:1), linoleic (18:2), and linolenic (18:3) acids [15]. The ratios of these to each other are important to the economic and nutritional value of the nut. Lower linoleic and linolenic acid content oils may have a longer shelf life, and monounsaturated fatty acids may be more desirable because of their potential health benefits [7, 12]. The high linoleic acid content of walnut oil makes it undesirable for use in cooking as it is more prone to charring. But walnuts also possess numerous polyphenolic compounds with potent free radical scavenging ability and therefore, capable to break the propagation chain of lipoperoxidation [13]. Walnuts are a perfect ingredient in a variety of breads, muffins, cakes, and biscuit.

High levels of polyunsaturated fatty acids make walnut oil prone to oxidation and may mean that oil has a limited shelf-life. Some experiments have been carried out on the oxidation stability of walnut oil. Temperature, light, moisture and exposure to oxygen have been found to be the main contributing factors to oxidation [6, 11, 13]. It was found that walnut oil stored at room temperature in the dark, in sealed bottles, showed only small rises in peroxide values after four months of storage and remained an acceptable product in terms of its sensory properties.

Oxidation of walnut lipids is linked to the appearance of unpleasant odors and flavors. Tocopherol isomers provide some protection against oxidation. Walnut oil, which is cold pressed from the meat of dried walnuts, has a strong and distinctive walnut flavor. It is generally used as a flavoring for baked goods and for some sauces. It can provide a bold flavor to salad dressing or it can be added to mildly flavored oils to create a subtle taste [8].

If the cold pressed walnut oil is to be effectively used in the food industry and human nutrition, it is important to determine how long it can be stored for without any deterioration. This storage trial was set up to determine the storage life of walnut oil. The quality of cold pressed walnut oil was assessed by measuring the primary and secondary oxidation products accumulation during 30 weeks of storage.

II. Materials and methods

2.1. Plant material

Walnut (*Juglans regia* L.) healthy fruits were manually collected in October 2011 in Chisinau, Central Moldova. The walnut fruits were stored at room temperature, packed in bags in order to protect them from light until extraction.

2.2. Walnut oil extraction

Prior to chemical analysis, the walnuts were manually cracked and shelled and then milled into a fine powder in an electric mill (Braun, Germany). Oil was extracted using cold pressing with an electrical lab press PSU - 125. General scheme of walnut oil extraction procedure is given in figure 1.

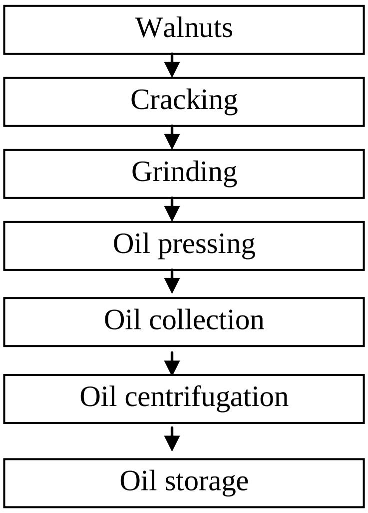

Figure 1. *Experimental scheme of cold pressed walnut oil obtaining.*

Extracted oil sample had a light yellow colour and very characteristic nutty flavour. Oil sample was collected, centrifuged and stored in dark polypropylene tube at 18±2 ^{0}C until analysis.

2.3. Chemical and reagents

Ethanol (99.9%), methanol (99%), potassium hydroxide, phenolphthalein, potassium iodide, sodium thiosulfate ($Na_2S_2O_3 \times 5H_2O$) and starch were supplied by Eco-Chimie (Chisinau, Moldova). Chloroform, 1-butanol and glacial acetic acid were purchased from Sigma-Aldrich. 2-thiobarbituric acid (4,6-dihydroxy-2-mercaptopyrimidine) and p-anisidine were obtained from Alfa Aesar. All the chemicals used were of HPLC or analytical grade. Distilled water was used throughout.

2.4. Peroxide Value

Oxidation rate was studied by determination of the peroxide value (PV). This was determined according to AOCS Official Method Cd 8-53 (AOCS, 2003). Peroxide value was expressed as millimoles peroxide per kilogram of walnut oil [3].

2.5. UV/Vis spectra analysis

The UV/Vis spectra were recorded using UV/Vis spectrophotometer HACH-LANGE DR-5000 (Germany) in the range of 200 - 750 nm using quartz cuvette 10×10 mm. Walnut oil sample was dissolved in isooctane. There were identified the maxima wavelengths specific for different compounds.

2.6. Conjugated dienes & trienes

The experiment was carried out according to the AOCS Official method Ti la 64 (AOCS, 1993) with minor modifications [1, 9]. Approximately 0,02 g of walnut oil was placed into a 25 ml volumetric flask. The sample was dissolved in chloroform, brought to volume and mixed thoroughly. Absorbance of the dissolved walnut oil was measured in UV/Vis spectrophotometer HACH-LANGE DR-5000 (Germany) at 232 nm and 270 nm using quartz cuvette 10×10 mm. Results were expressed in micromole conjugated dienes/trienes per gram of walnut oil.

2.7. p-Anisidine Value

The p-anisidine value of walnut oil samples was measured following the methodology described in AOCS Official Method Cd 18-90 (AOCS, 1997) [2, 10]. This value was determined by the amount of aldehydes (principally 2-alkenals and 2,4-dienals) in walnut oil samples after reaction in an acetic acid solution of the aldehydic compounds in the walnut oil and the p-anisidine mixture. Absorbance of the samples was measured in UV/Vis spectrophotometer HACH-LANGE DR-5000 (Germany) at 350 nm using quartz cuvette 10×10 mm.

2.8. 2-Thiobarbituric acid Value

The 2-thiobarbituric acid was determined according to the AOCS Official Method Cd 19-90 (AOCS, 2009) [4]. The method is based on the spectrophotometric quantitation of the pink complex formed after reaction of one molecule of malondialdehyde (MDA), product of oxidation, with two molecules of 2-thiobarbituric acid added to the walnut sample.

2.9. Statistical analysis

Variance analysis of the results was carried out by least square method with application of coefficient Student and Microsoft Office Excel program version 2007. Differences were considered statistically significant if probability was greater than 95% (p-value <0,05). All assays were performed by triplicate at room temperature 20 ± 1 ^{0}C. Experimental results are expressed as average ± SD (standard deviation).

III. Results and discussion

Today, fats and oils products are developed and subsequent production controlled with a knowledge of their composition, structural and functional properties, and the expected reactions obtained through the application of scientific research. Progress in the utilization of fats and oils for the production of useful products is dependent upon a thorough knowledge of the characteristics of the raw materials, the changes effected by each process, and the requirements of the individually prepared food product. Physical, chemical, and performance analyses are the tools available to fats and oils processors for the purchase of raw materials, development of new products, and evaluation of the products produced.

In this work walnuts as a perspective and valuable raw material were proposed for oil extraction. Walnuts chemical composition is presented in figure 2.

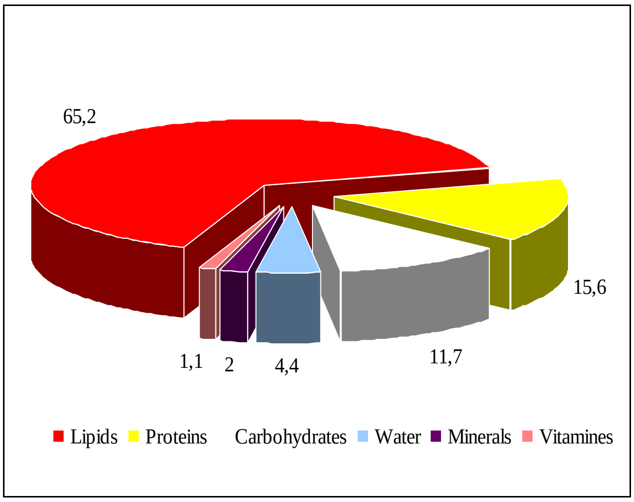

Figure 2. *Chemical composition of walnuts*

It is important to note, that walnut lipids contain high amount of polyunsaturated fatty acids: linoleic (18:2) and linolenic (18:3), which contribute to its biological and nutritional value. But on the other side, this makes it prone to oxidation.

The health benefits of walnut oil are attributed to its chemical composition. Walnut oil contains approximately 7% saturated, 20% monounsaturated and 73% polyunsaturated fatty acids [16]. These high levels of polyunsaturated fatty acids make walnut oil prone to oxidation and may mean that oil has a limited shelf-life, i.e. nutritional and organoleptic changes due to losses of essential fatty acids and formation of volatile compounds from subsequent degradation of hydroperoxides.

Oxidation is a radical chain reaction. After an induction period, it may run very fast under certain circumstances. A chemical attack on the alkyl group is followed by a chain reaction, resulting in a hydroperoxide group (-OOH) in the chain. The chain reaction is started by peroxy-, alkoxy- and alkyl-radicals:

$$R\text{-}OO^{\bullet},\ R\text{-}O^{\bullet},\ R^{\bullet} \tag{1}$$

The chain reaction proceeds by reaction with oxygen or RH:

$$R^{\bullet} + O{=}O + R\text{-}OO^{\bullet} \tag{2}$$
$$R\text{-}OO^{\bullet} + R\text{-}H + R\text{-}OOH + R^{\bullet} \tag{3}$$
$$R\text{-}O^{\bullet} + R\text{-}H + R\text{-}OH + R^{\bullet} \tag{4}$$

It is accelerated by branching of the chain:

$$R\text{-}OOH + R\text{-}O^{\bullet} + {}^{\bullet}OH \tag{5}$$
$$2\ R\text{-}OOH + R\text{-}O^{\bullet} + R\text{-}OO^{\bullet} \tag{6}$$

The chain reaction ends by combination of two radicals. It is well known, that this negative reactions can be stopped by the antioxidants.

In this study, UV/Vis spectra of the investigated walnut oil were analyzed in the wavelength range of 200 - 750 nm (Figure 3).

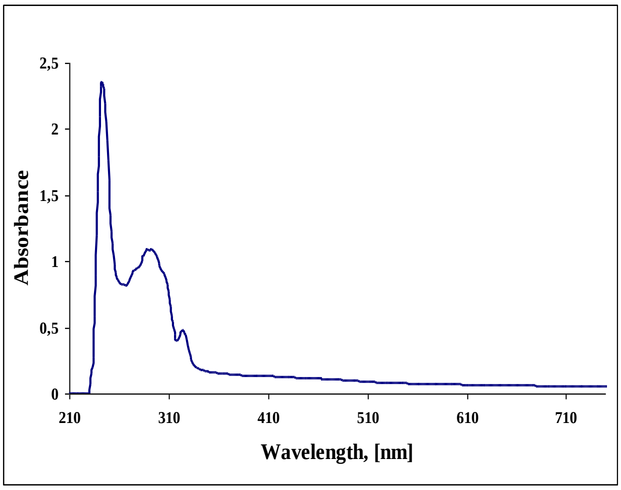

Figure 3. *UV/Vis spectra of cold pressed walnut oil*

From identification of bioactive compounds by UV/Vis spectra, it clearly revealed that walnut oil contains juglone (245 nm), tocopherol (295 nm) and retinol (325 nm). Probably, these compounds can play protective role in oxidation process of walnut oil.

Oxidation of lipids is a major cause of their deterioration, and hydroperoxides formed by the reaction between oxygen and the unsaturated fatty acids are the primary products of this reaction. Hydroperoxides have no flavor or odor but break down rapidly to form aldehydes, which have a strong, disagreeable flavor and odor.

The peroxide concentration is a measure of oxidation or rancidity in its early stages. But peroxide determination does not provide a full and unqualified evaluation of oils flavor because of the transitory nature of peroxides and their breakdown to nonperoxide materials. Therefore, conjugated dienes and trienes content were evaluated parallel with peroxides concentration. Experimental results are presented in figure 4.

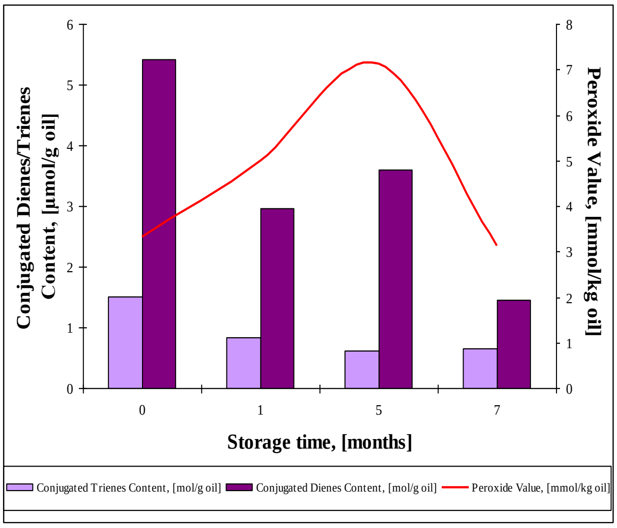

Figure 4. *Primary oxidation products accumulation in walnut oil during storage*

It is well known, that primary oxidation products of vegetable oils are peroxides, which can be transformed induced by environmental factors such as humidity, temperature and oxygen content into secondary oxidation products such as aldehydes, ketones, oxidized fatty acids and other compounds.The oil quality data from walnut kernels pressed at cold indicated variations for all parameters evaluated, including peroxide values. It can be explained, that peroxides represent unstable intermediate compounds of lipid oxidation process. These trends were registered for conjugated dienes content of the investigated walnut samples

The hydroperoxides formed react further to aldehydes, ketones and fatty acids, all of which represent secondary oxidation products and nefatively influence on oil quality. Anisidine value is a measure of secondary oxidation (the amount of α and β unsaturated aldehydes), and therefore is useful in determining the quality of oils and the efficiency of processing procedures. Changes in secondary oxidation products accumulation were expressed by p-anisidine and 2-thiobarbituric acid values. Obtained experimental results of p-anisidine values in walnut oil samples are shown in figure 5.

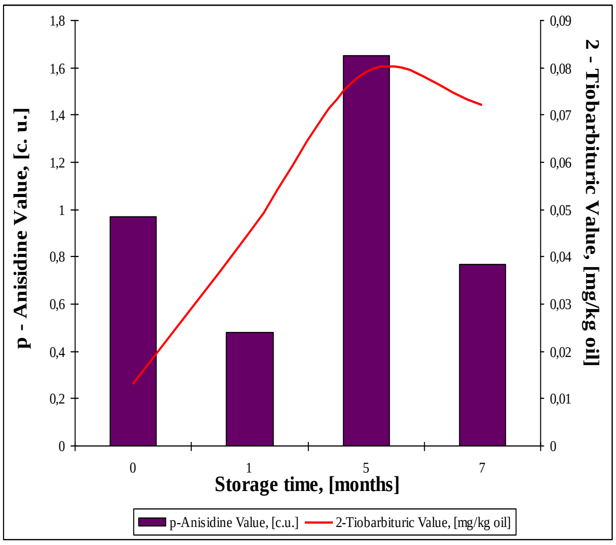

Figure 5. *Secondary oxidation products accumulation in walnut oil during storage*

As can be seen from figure 5, there were evaluated 2-tiobarbituric value of walnut oil sample as an important indicator of secondary oxidation products accumulation. Significant increase of p-anisidine and 2-tiobarbituric values were registered after 5 months of walnut oil storage.

For better understanding of obtained experimental results there was calculated total oxidation value (TOTOX) for walnut oil sample. TOTOX value represents the sum of primary (peroxides) and secondary (aldehydes) oxidation products accumulation in vegetable oils. To compare the influence of storage time on the oxidation process of cold pressed walnut oil, changes in TOTOX value are indicated in figure 6.

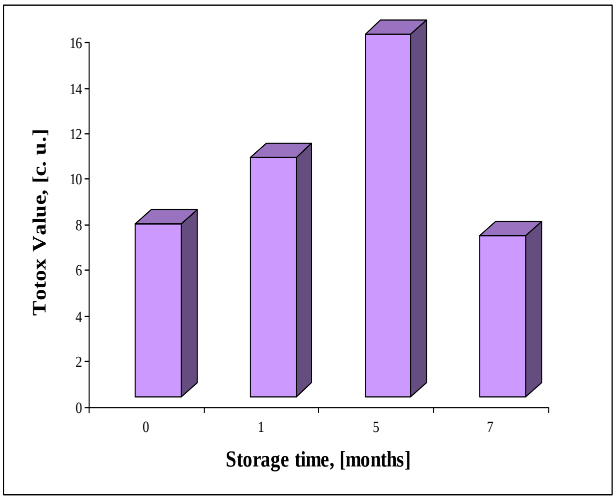

Figure 6. *Changes in TOTOX value of walnut oil during storage*

TOTOX value represents the sum of primary (peroxides) and secondary (aldehydes) oxidation products accumulation in vegetable oils. It is obvious, that increasing of storage time of cold pressed walnut oil leads to an increase of the TOTOX value.

IV. Conclusions

Today, walnut oil has been extracted on a small scale to obtain edible vegetable oil in Europe. However, walnuts can be used to produce high quality vegetable oil. The results of this research showed the influence of storage time on the intensity of primary and secondary oxidation products accumulation in cold pressed walnut oil. It was demonstrated that walnut oil retains acceptable quality after 7 months of storage. It is important to underline, that obtained results of this study are intermediate and could help authors to describe the scheme of walnut oil oxidation process and also to elaborate improved technology for walnut oil stabilization.

Acknowledgments

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METHOD OF INITIAL PARAMETERS IN THE DYNAMIC ANALYSIS OF MACHINE ELEMENTS FOODSTUFF INDUSTRIES

J.N. Petrova, I.V. Zhdanov, D.O. Kristya

Donetsk national university of economics and trade named after Mykhayilo Tugan-Baranovsky,

Abstract. *Stress-deformed state of vibration machine rollers under dynamic force was analyzed in the article. The method of original parameters for inertia strength, bending moment and the masses movement definition was used.*

Keywords: *dynamic loads, vibrating machines, method of initial parameters, bending moments.*

Statement of the problem and its relationship with the most important scientific and practical tasks

Vibration machines are used in the food industry in various technological processes: screening, separation, washing, transporting, crushed formulation, dosing and others.

Vibratory equipment containing complex of mechanical systems that undergo with dynamic load effects. In the academic and professional literature, there are virtually no guidance on dynamic analysis of elastic rod systems including vibration machines [1], or calculations that are reduced to the determination of vibrate and compute frequencies of working groups vibration [2, 3] and most intact are remaining calculations issues on the strength of systems with distributed parameters and lumped masses including disturbing force and inertia.

Article aims at teaching of dynamic analysis of vibrating systems by the initial parameters.

The main material

The most widely used vibrating machines that are operative when working body machines performs harmonic oscillations.

As is known [6], the stress - strain state of elastic systems vary according to their kinematic characteristics.

If weightless system with one degree of freedom has disturbing load $q(x,t)$, the displacement equation of elastic system curved axis has the form:

$$y(x,t) = -\delta_{11} M\, \ddot{y}(x,t) + \int_0^l \delta_{1x} q(x',t)\,dx' , \qquad (1)$$

where: δ_{1x} – the movement of a point of mass, δ_{11} – mass displacement of a single force applied at the point of securing supply.

Now we can obtain the differential equation of motion

$$\ddot{y}(x,t) + \omega^2 y(x,t) = \omega^2 \int_0^l \delta_{1x} q(x',t)\,dx' = f(t). \quad (2)$$

Its decision makes sense to look for in the form of the eigenfunctions of the Fourier method [7].

In the case of harmonic loading on the strength $P(t) = P \sin\theta t$ or the time $\tilde{M}(t) = \tilde{M} \sin\theta t$ it is not necessary to find a solution in the form of a series because series are the sum of harmonics expanded in Fourier series of load. But the harmonic load is already harmonic. Therefore, we can apply the method of initial parameters. Equation of curved axis beam with bending stiffness EI by the method of initial parameters of the form [4]:

$$y(x) = y_0 + y_0' x + \frac{P_0 x^3}{6EI} + \frac{M_0 x^2}{2EI}, \qquad (3)$$

where the zero index is marked with the initial deformation and strength parameters.

Initial parameters are determined from the boundary conditions at the ends of the beam.

Assuming that the variable time t obeys the harmonic law, we can obtain displacement on the function of two variables – flowing coordinate x and time t.

$$y(x,t) = y(x)\sin(\omega t + \mu). \qquad (4)$$

The oscillation frequency is found in the process of solution, and the initial phase is determined from the initial conditions of perturbation fluctuations of the initial deviation from the equilibrium position and initial velocity

$$\operatorname{tg}\mu = \frac{y_0}{v_0}\omega . \qquad (5)$$

Let’s count equation (1) to the elastic fastening systems for bearings and find initial parameters that determine the equation of motion of the masses and give the opportunity to find the forces of inertia that must be considered along with a static load. After determining the displacement $y(x,t)$ we can determine the strength of inertia.

$$P_i = -M\,\ddot{y}(x,t) = M\theta^2 y(x,t)\sin\theta t =$$

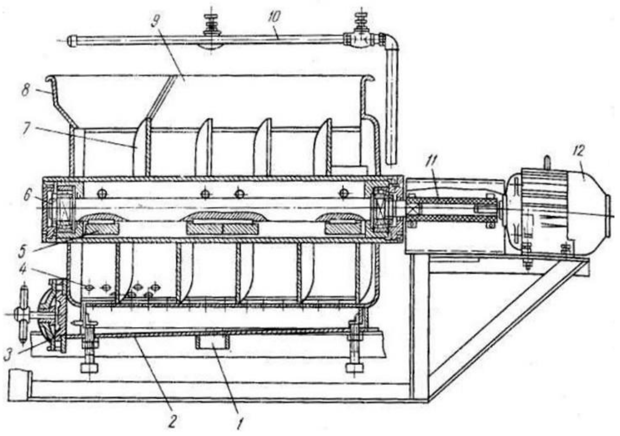
$$= \frac{\delta_{1p}}{\delta_{11}} v\delta^2 P\sin\theta t , \qquad (6)$$

where: $\delta = \theta / \omega$ - the ratio of the perturbation frequency θ to natural frequency ω, and v – coefficient of fluctuations growth.

Isolated coefficients δ_{11} and δ_{1P} we can obtain determine by Vereshchagin rule [8].

Thus the tasks for the forced oscillation of harmonic load can be solved by the method of initial parameters for monotonic loading system [5] by inertia forces of concentrated masses, given the amplitude of disturbing loads and cargo system.

Here is an example of a dynamic calculation of the elements of vibration equipment which undergoes a significant bending deformation - a shaft of washing machine MMKV-2000. Mechanical properties of materials determine rigidities of washing and accordingly design washing machines features (Figure 1).



1 – drain pipe; 2 – tray; 3 – hatch; 4 – vents; 5 – unbalances; 6 – shaft; 7 – auger; 8 – loading slot; 9 – box; 10 – water supply pipe; 11 – flexible clutch; 12 – electric motor

Figure 1 – *Vibrating washing machine MMKV - 2000*

Oscillatory movements of working machine body (9) are carried out due to rotation of the central part of the shaft (6) with the unbalance (5). Fixing shaft is carried in two bearings contained in the ends of the inner cylinder. Shaft movement rotating it receives from an electric motor through the clutch (11), closed with metal casing. Working chamber is the space between the inner surface of the cylindrical shell and the outer surface of the cylinder, where shaft is rotating.

Diagram shown in Figure 2.

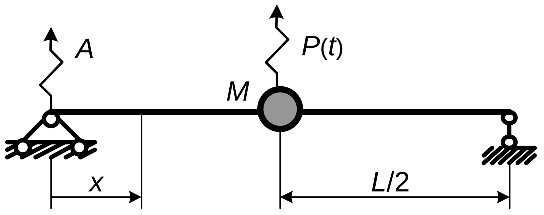


Figure 2 – *Diagram*

Using the method of initial parameters, we can draw equation of shaft curved axis for washing machines in steady motion

$$y(x,t) = y(x)\sin\theta t , \qquad (7)$$

where, according to the formula (3)

$$y(x) = y_0' x + \frac{Ax^3}{6EI_z} . \qquad (8)$$

By the differentiation we find:

$$y'(x) = y_0' + \frac{Ax^2}{2EI} . \qquad (9)$$

Bending moment in the intersection x: $M(x) = Ax$. Transverse force: $Q(x) = A$.

Amplitude value of the inertia weight force, which varies, according to the formula (6):

$$P_i = -M\,\ddot{y}(l/2) = M\theta^2\left(y_0' \frac{l}{2} + \frac{Al^3}{48EI_z} \right).$$

Dynamic initial parameters determined from

$$y'(l/2) = 0 ,\; Q(l/2) = -\frac{P}{2} - \frac{P_i}{2} :$$

$$y_0' + \frac{Al^2}{8EI_z} = 0,$$

$$A = -\frac{P}{2} - M\theta^2 y_0' \frac{l}{4} - M\theta^2 \frac{Al^3}{96EI_z}.$$

Other words, we obtain the system of equations:

$$\begin{cases} y_0' + \dfrac{Al^2}{8EI_z} = 0, \\ y_0' M\theta^2 \dfrac{l}{4} + A\left(1 + M\theta^2 \dfrac{l^3}{96EI_z}\right) = -\dfrac{P}{2}. \end{cases}$$

The main determinant of this system

$$Det = 1 + M\theta^2 \frac{l^3}{96EI_z} - M\theta^2 \frac{l^3}{32EI_z} =$$
$$= 1 - M\theta^2 \frac{l^3}{48EI_z}.$$

Therefore, the natural frequency of vibration is

$$\omega = \sqrt{\frac{48EI}{Ml^3}}.$$

The main determinant can now be written as:

$$Det = 1 - \frac{\theta^2}{\omega^2} = 1 - \delta^2 = \frac{1}{v}.$$

From the system nonhomogeneous equations we can find initial parameters:

$$y_0' = \frac{Pl^2}{16EI_z} v, \quad A = -\frac{P}{2} v.$$

The deflection in the middle of the beam:

$$y(l/2) = y_0' \frac{l}{2} + \frac{Al^3}{48EI_z} = \frac{Pl^3}{48EI_z} v = v\delta_{11} P.$$

Given the maximum static load – shaft deflection:

$$y_{\max} = \frac{Ql^3}{48EI_z} + \frac{Pl^3}{48EI_z} v =$$
$$= \frac{Ql^3}{48EI_z}\left(1 + \frac{P}{Q} v\right) = fk_D.$$

Dynamic force can be determined by the deflection:

$$P_D = \frac{y(l/2, t)}{\delta_{11}} = vP \sin \theta t.$$

It consists of inertial forces:

$$P_i = M\theta^2 y(t) = M\theta^2 v\delta_{11} P \sin \theta t = v\delta^2 P \sin \theta t$$

and applied disturbing force $P \sin \theta t$, so:

$$P_D = P\left(1 + v\delta^2\right) \sin \theta t = P\left(1 + \frac{\delta^2}{1 - \delta^2}\right) \sin \theta t =$$
$$vP \sin \theta t.$$

Considering the static loading, calculated bending moment is:

$$M_{\max} = \frac{Ql}{4} + \frac{Pl}{4} + \frac{P_i l}{4} = \frac{l}{4}\left[Q + P\left(1 + v\delta^2\right)\right] =$$
$$= \frac{l}{4}\left[Q + P\left(1 + \frac{\delta^2}{1 - \delta^2}\right)\right] = \frac{Ql}{4}\left(1 + \frac{P}{Q} v\right) = M_S k_D.$$

Now, by the strength condition:

$$\sigma = \frac{M_{\max}}{W_z} \le [\sigma]$$

it is possible to obtain projecting or checking calculations.

Conclusions

Thus the committed stressed-strained state of the washer MMKV-2000 vibration shaft showed that the flexible vibration machine system with discrete masses must rely on the method of initial parameters for dynamic load, which includes the effect of inertial forces, the effect of disturbing forces which are focused on mass and static loading

Prospects for further research in this direction are the analyzing of the flexible systems stress-strain state of manufacturing and food processing equipment with distributed parameters, variable deflections, torsional vibrations, which are much more complex, so they will be discussed in further publications of the author.

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RESOURCE-SAVING TECHNOLOGY OF SEMI-FINISHED GOODS TO LONG STORAGE OF PLANT AND ANIMAL MATERIALS

E. Popov[1], N. Rodionova[1], S. Stefanov[2],
T. Bakhtina[1]

[1] *Voronezh State University of Engineering Technologies, 19, Revolution Blvd., 394036,*
Voronezh, Russia, e-mail: e_s_popov@mail.ru
[2]*University of Food Technologies, 26, Maritsa Blvd., 4002, Plovdiv, Bulgaria,*
e-mail: stvstefanov@mail.ru

Abstract. *A promising direction in the development of engineering and technology, the food industry is the use of low-temperature etsya Hygrothermal cooking raw with preliminary evacuation. The technology allows you to maintain vitamins, proteins, carbohydrates, fats, macro - and micronutrients raw materials in the native state, and also protects the food from undesirable organoleptic changes occurring in the traditional thermal processing, while maintaining attractive consumer product quality and safety guaranteed hygiene throughout shelf life [1, 2, 3].*

Key words: animal feed, vegetable raw materials, intermediate products, microbiological safety, vacuum packaging, low temperature heat treatment.

In cooking, as a rule, use a variety of products that provide a balanced composition of the finished product on the fats, proteins, carbohydrates, macro-and micronutrients. In cooking, a combination of common rice, raw vegetables: onions and carrots, and aquatic organisms: fish, squid, which allows you to get a dish with high consumer properties.

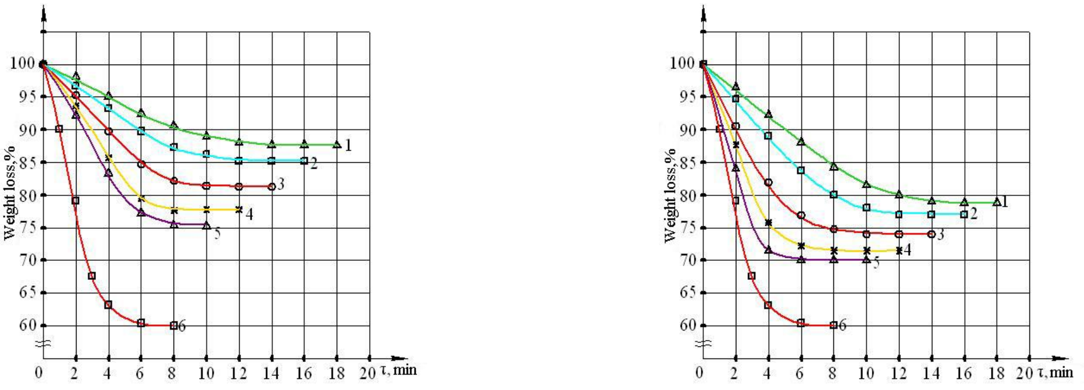
In order to determine the optimum operating parameters of the technological process of hygrothermal processing of culinary products with pre-vacuum packaging to a comprehensive study of each individual component specialties. Based on these data can predict relations component of food that provides efficient power consumption, minimization of process losses of mass, as well as the achievement of high quality indicators of culinary products and increase shelf life.

The objects of study were selected following prescription ingredients: onions (cut cube 0,5×0,5 cm), carrots (cut into strips 1,5×0,2×0,2 cm), long grain milled rice, as well as squid and carp (fillet with skin, boneless, sliced, portioned pieces weighing 40 g).

Experimental Study of hygrothermal treatment was conducted under convective heat transfer fluid with moisture from 0 to 100%, in terms of temperature control fluid in the chamber apparatus in the temperature range 333 ... 373 K. The samples were pre-packaging in vacuum polymeric packages followed by heat cooking. Packaging is made with vacuum - packing machine Besser vacuum, series FAVORIT, with the final pressure of 200 Pa, at a thickness of 140 microns polyethylene film.

In samples of the product during processing hygrothermal control the degree of culinary readiness every 30 seconds until constant weight of the samples at the same time the allocation of a constant amount of juice. As a control, the samples examined, treated under the same temperature conditions without packaging, as well as samples, cooked in the traditional way.

Analysis of experimental data showed that the process loss of packaged food samples examined have smaller numerical values compared with unpackaged samples: samples of squid – 12,5 ... 24,5%, 21,0 ... 29,5%; for samples of carp – 9,5 ... 20,0%; 16,0 … 26,5%; for samples of onion – 11,5 ... 26,0%; 16,5 ... 29,5%; for samples of carrots 6,5 ... 19,0%; 11,5 ... 24,0% - respectively in the studied temperature range 333 ... 373 K [1, 2, 5]. Graphic changes depending on weight of packaged samples of squid on the duration of heat cooking in Fig. 1. Analogous relationships were obtained for the samples of carp, onions and carrots.



a b

Figure 1. *Dependence of the change in mass of packed samples of squid on the length of the STP-heat cooking (at different temperatures)*
a - packed samples, b - unpackaged samples
1 - 333 K, 2 - 343 K, 3 - 353 K, 4 - 363 K, 5 - 373 K, 6 - Traditional way processing

The pilot study was to investigate the effect of temperature on the Duration of the process of heat treatment of the samples. Found that the duration of the process of heat treatment to achieve culinary readiness adiabatically depends on the temperature (Fig. 2). With increasing temperature (from 333 K to 373 K) heat cooking time is reduced: for samples of squid - from 17 to 5 minutes and from 15 to 4 minutes for samples of carp - from 13 to 5 minutes, and from 10 to 4 minutes for carrot samples - from 44 to 20 minutes and from 32 to 15 minutes for samples of onions - from 28 to 14 minutes, and from 21 to 10 minutes, respectively, for packaged and unpackaged samples [1, 2, 5].

It was found that the degree of hydration of the tissues of aquatic organisms decreases with increasing treatment temperature.

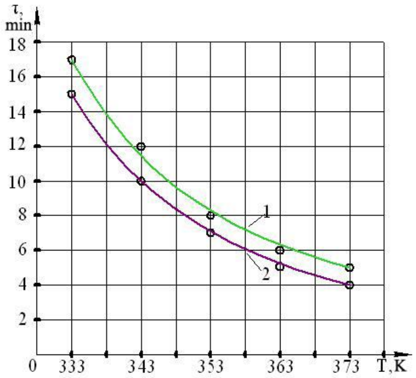


Figure 2. *Dependence of heat-STI sample processing of squid samples at temperature: 1 - packed; 2 – unpackaged*

Thus at T = 333 K, it is 3,2, 2,18 - packaged samples of squid and carp; 2,7; 1,95 - for unpackaged samples squid and carp, at T = 373 K – 2,5; 1,84 and 2,3; 1,63, respectively. With increasing temperature, the difference in the numerical values of the degree of hydration is reduced (Fig. 3). The degree of hydration of tissues in the control samples was 2,11 and 1.51 - sample squid and carp [1, 2].

In determining the optimum conditions hygrothermal processing with a preliminary vacuum packing one of the objects of the study was long-grain milled rice.

It is known that pre-hydration provides rice to reduce the time in the following heat treatment. Therefore, the test samples were subjected to preliminary hydration and packaging in vacuum plastic bags with subsequent heat cooking treatment [4].

It was found that the temperature of pre-hydration has a significant effect on the duration of the thermal treatment (Fig. 4). So by increasing the temperature of hydration prior samples of rice from 323 to 373 K, the reduction in the duration of heat treatment at 2,2 ... 2,5 times for the temperature range 353 ... 373 K.

In the course of study is determined by the amount of moisture needed to reach the desired consistency of the mixture components, increasing the yield of finished products, in ensuring maximum shelf life, which is known to be largely determined by the amount of free moisture in a food facility.

The test objects were considered rice-vegetable mixture with hydrobionts with the following ratios of the components: for rice-vegetable mixture with squid: rice hydrated - 58%, onion - 12%, squid - 30% for rice-vegetable mixture with carp: rice hydrated - 60%, carrot - 6%, onions - 9%, fish - 25%.

Hygrothermal process food processing components were carried out in the temperature range 333 - 373 K, with pre-vacuum packing in plastic sheeting, water content of the coolant was maintained at 100%.

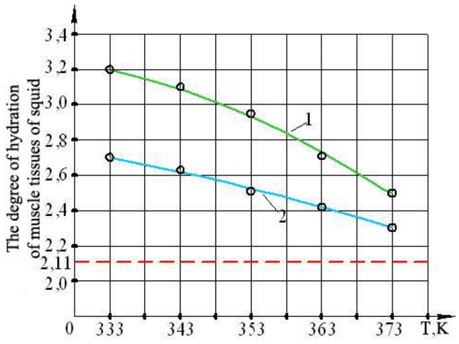


Figure 3. *Dependence of the degree of change hydration of the muscle tissue of squid on the temperature of treatment:*
1 - packed 2 - unpackaged

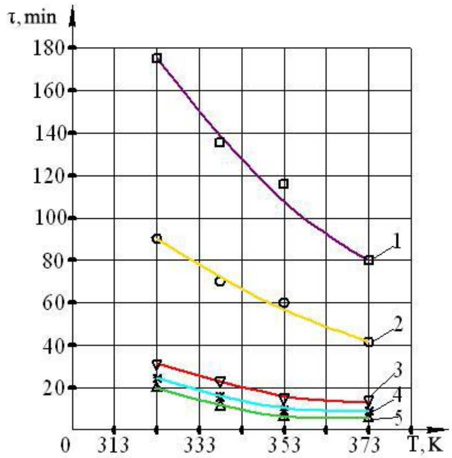
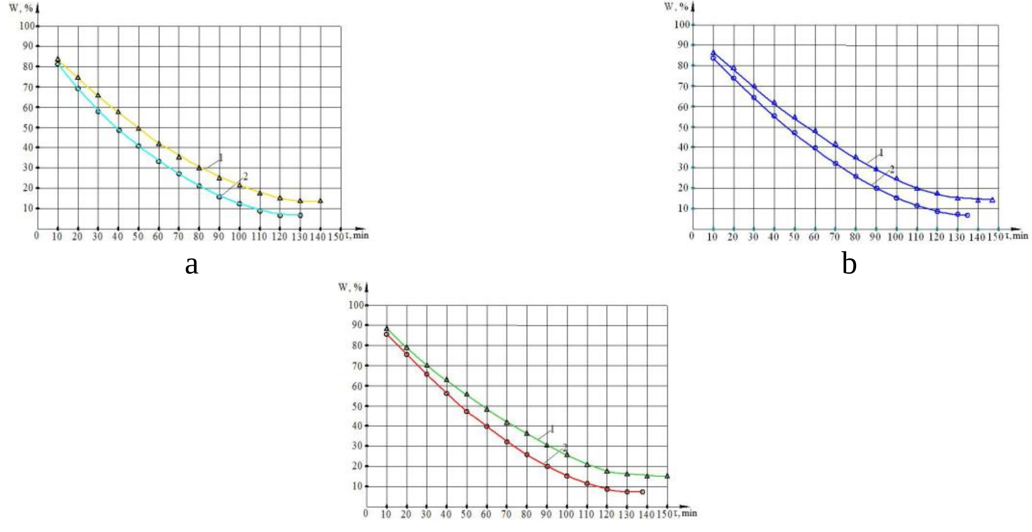


Figure 4. *Dependence of rate of rice samples heat cooking processing from the pre-hydration temperature at treatment temperatures:*
1 – 353 К, 2 – 358 К, 3 – 363 К, 4 – 368 К,
5 – 373 К

Change in the state of moisture in the product has an effect on the physically-chemical and sensory characteristics of products. In connection with this research was to determine the impact of this technology on the regime change in the form of moisture due to the object of study. Moisture range is from 0 (control) to 15,0 % by weight.

In the treated experimental samples studied the dynamics of change in the humidity hygrometer FD - 610 «KETT» (Japan) at intervals of 2 min. Quantitative and qualitative changes in forms of communication were analyzed for moisture basis of graphic dependences dehydration and dehydration rate samples of dishes with squid (Fig. 5, 6) and carp (similar dependence).



a

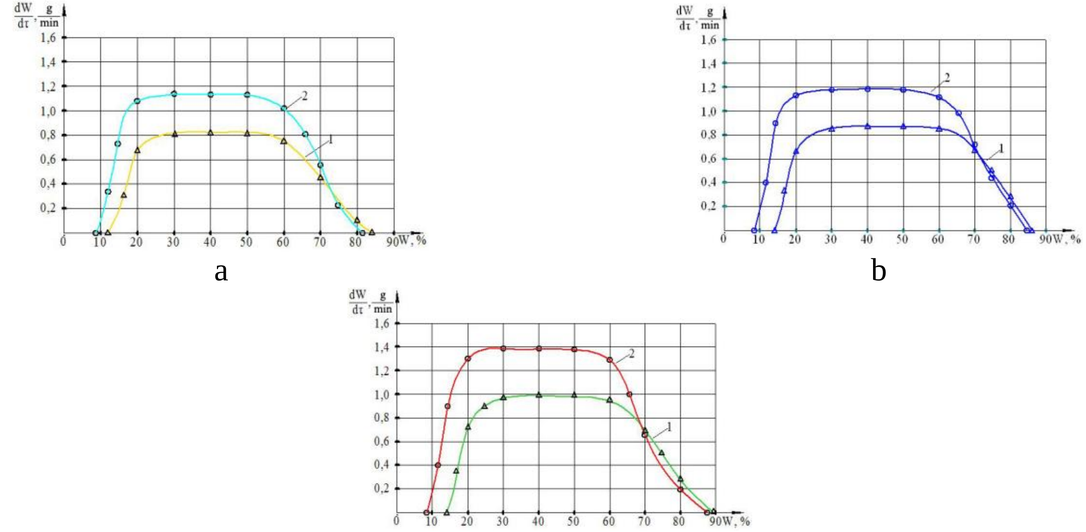
b

c

Figure 5. *Graphics depending dehydration of sample rice-vegetable mix with squid (a - without water; b - with the addition of water (12,5%); c - with the addition of water (15,0%)) treated at different temperatures :*
1 - 333 K, 2 - 373 K

Based on the analysis of the dependencies, that the duration of the process of dehydration rice-vegetable mixtures hydrobionts increases with the addition of water and makes up for rice-vegetable mixture with squid: 135 (at 373 K) - 145 minutes (at 333 K) and 142-145 (at 373 K) - 153-157 minutes (at 333 K), for rice-vegetable mixture with carp: 130 (at 373 K) - 140 minutes (at 333 K) and 135-138 (at 373 K) - 147-150 minutes (at 333 K).

In analyzing the graphic dependences of dehydration (Fig. 6) revealed that there are three stages of dehydration: increasing (warm-up), constant and decreasing speed of the process. This indicates the presence of moisture in the product in a variety of forms: a period of constant velocity corresponds to dehydration process of removing free water, the period of decreasing rate - the process of removing the bound form of moisture.



a

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Figure 6. *Graphic dependence of the rate of dehydration of the samples rice-vegetable mix with squid (a - without water; b - with the addition of water (12,5%); c - with the addition of water (15,0%)) treated at different temperatures: 1 - 333 K, 2 - 373 K*

It was found that the temperature of the thermal treatment of a humid rice-vegetable mixtures hydrobionts, and the amount of overhead water have a significant effect on the transition of the free moisture in a bound state. Dehydration speed changes in the following ranges: for rice-vegetable mixture with squid: from 0,90 to 1,22 g / min (333 K, 373 K) - for samples of dishes prepared without the addition of water, from 0,95 to 1, 53 g / min (333 K, 373 K) - for samples of dishes prepared with the addition of water in different proportions, for rice-vegetable mixture with carp, from 0.84 to 1.16 g/min (333 K, 373 K) - for samples of dishes prepared without the addition of water, from 0,86 to 1,39 g/min (333 K, 373 K) - for samples of dishes prepared with the addition of water in various proportions.

From the analysis of the influence of the amount of applied water at the ratio of free and bounded moisture in the samples compared to the control, it was found that the rice-vegetable mixture with squid addition of water in excess of 12,0% of the total weight of food leads an increase in the mass fraction of free water. For rice-vegetable mixture with carp introduction of additional water is not recommended since the introduction of water even in an amount of 5% of the total weight of food leads to an increase of mass fraction of free water.

It should also be noted that a further increase in the amount of water in the recipe, before the heat treatment, leading to a decrease in organoleptic and shortened shelf life of rice-vegetable mixture to aquatic organisms.

Based on these data the ratio of adjusted prescription components for rice-vegetable mixture with squid, which are: rice hydrated – 54,0%, onion – 11,0%, squid - 27,0%, water – 8,0% . For rice-vegetable mixture with carp ratio prescription components remained unchanged.

On the basis of research on heat - humid processing components of these mixtures was found that the heat treatment of foods should be carried out in the temperature range 363 - 368 K, with a preliminary vacuum packing in plastic sheeting and water content of the coolant at 100%. In samples of the product to control the degree of culinary readiness, defined achievement required consistency of the finished product.

The duration of heat cooking, to achieve the degree of culinary readiness, were: for rice-vegetable mixture with squid - 9 min and rice-vegetable mixture with carp - 11 min.

In the study of combined products were determined mass fraction of protein, fat, carbohydrate, vitamins, minerals, amino acid composition, the difference coefficient amino acids, biological value, acid and peroxide value. To determine the benefits of the developed method of cooking as a test of the sample studied the mixture of the same composition, cooked with steam without packing at 368 K. The experimental data are presented in Table 1.

Table 1 - *Performance of biological value of rice-vegetable mixtures hydrobionts*

Item	**Rice-vegetable mixture with squid**		**Rice-vegetable mixture with carp**	
	Sample treated in the traditional way	Packed sample treated in the combi steamer	Sample treated in the traditional way	Packed sample treated in the combi steamer
Physical and chemical properties				
Protein content,%	19,02	23,06	27,06	30,27
Fat content,%	0,68	0,58	18,34	21,53
Mass fraction of carbohydrates,%	52,13	60,44	52,32	60,44
Acid number, mg KOH / g	-	-	1,94	1,02
Peroxide value, %J_2	-	-	0,03	0,03
Zinc, mg/kg	8,7	9,3	9,2	10,1
Copper, mg/kg	1,9	2,1	2,2	2,3
Manganese, mg/kg	0,25	0,28	0,31	0,33
Vitamin A, mg/kg	1,1	1,7	4,2	6,8
Vitamin B_1, mg/kg	0,17	0,31	0,19	0,38
Vitamin B_2, mg/kg	0,95	1,55	0,90	1,58
Vitamin C, mg/kg	6,10	10,5	6,0	11,0
Vitamin $Д_3$, mg/kg	1,25	2,2	1,10	2,6
Vitamin PP, mg/kg	723,5	944,1	714,7	945,2
The amino acid composition				
Isoleucine	5,40	4,62	4,35	5,97
Leucine	12,37	14,0	13,71	13,72
Lysine	12,02	12,69	15,05	13,67
Methionine + cystine	4,69	5,19	5,50	8,4
Phenylalanine + tyrosine	9,05	9,41	11,95	11,97
Threonine	5,85	5,7	7,34	7,12
Valine	5,87	5,24	6,86	7,74
Tryptophan	1,24	1,25	1,20	1,21
Indicators of biological value				
Ratio of amino acid differences soon (RED),%	17,30	18,20	22,50	23,60
Biological value,%	75,10	81,80	71,10	76,20
Coefficient of utility (U),%	0,77	0,78	0,72	0,73
Figure comparable redundancy of essential amino acids (σ_c), %	10,14	9,83	12,45	12,02
Utilization rate of protein (C_{pu}), %	78,50	78,0	73,45	73,0

Analyzing the data in Table 1, it can be noted that the numerical values of indices reach their maximum values in the samples packaged rice-vegetable mixes, processed at low temperature heat treatment. Thus, the data give a mixture possess a high content of vitamins (25%), minerals (15%), protein, and fat (10%).

Table 2 - *Changes in the microbiological safety of rice-vegetable mixtures hydrobionts in storage*

Item	Rice-vegetable mixture with squid					Rice-vegetable mixture with carp				
	Sample treated in the traditional way		Packed sample treated in the combi steamer			Sample treated in the traditional way		Packed sample treated in the combi steamer		
	Storage time, day (with T=298±0,1 K)									
	1	2	1	5	7	1	2	1	5	7
Colony-forming unit, CFU/g	$4,5 \times 10^3$	$2,1 \times 10^5$	less than $1,0 \times 10^1$	$2,4 \times 10^2$	$4,5 \times 10^4$	$3,2 \times 10^3$	$4,4 \times 10^5$	less than $1,0 \times 10^1$	$4,1 \times 10^2$	$3,6 \times 10^4$
	Storage time, day (with T=276±0,1 K)									
	1	2	5	10	15	1	2	5	10	15
	$7,7 \times 10^1$	$8,9 \times 10^3$	$2,2 \times 10^1$	$1,6 \times 10^3$	$4,2 \times 10^4$	$5,4 \times 10^1$	$7,5 \times 10^3$	$3,4 \times 10^1$	$2,7 \times 10^3$	$4,7 \times 10^4$

Studies in rice-vegetable mixture with hydrobionts studied organic change nolepticheskih indicators microbiological safety during storage at temperatures: 276±0,1 К и 298±0,1 К.

In the samples rice-vegetable mixtures hydrobionts during storage, study of aerobic and facultative anaerobic microorganisms, Escherihia coli, Staphylococcus aureus, Clostridium perfringens and Listeria monocytogenes. Results are presented in Table 2.

Analyzing the data in Table 2, we can conclude that for the experimental rice-vegetable mixtures hydrobionts time to reach critical values of aerobic and facultative anaerobic microorganisms, hazardous to the health of the consumer (5×10^4 colony-forming unit (CFU/g) depends on the temperature conditions of storage. So much for the samples, the storage temperature which was T=298±0,1 К, time to reach the critical values of aerobic and facultative anaerobic microorganisms in two times less than for the samples with temperature storage T=276±0,1 К, i.e. 7 and 15 days.

In the control samples during the critical value aerobic and facultative anaerobic microorganisms, was 24 and 48 hours at a temperature storage T=298±0,1 и T=276±0,1 К respectively. During the study period of storage in the experimental samples were not detected: Escherihia coli, Staphylococcus aureus, Clostridium perfringens and Listeria monocytogenes.

Conclusions

Analyzing the experimental data, we can conclude that the use of low-temperature heat cooking food with a preliminary vacuum packing, allowing processed foods increase the performance of the biological value of 10-15%, in addition to save 20-25% of the vitamins, minerals 10-15% and to ensure the preservation of safety at the required level without special cooling product 6 - 7 days, with the result that the product can be recommended for special nutrition (tourism, expeditions, emergency situations, etc.).

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STORAGE STABILITY ASSESSMENT OF WALNUT OIL

E. Sandulachi, E. Chirita, V. Costis

Faculty of Technology and Management in Food Industry, Technical University of Moldova,
168, Stefan cel Mare Street, MD 2004 - Chisinau, Moldova, e-mail: luiza.sandulachi@gmail.com

Abstract. *This paper includes a bibliographic and experimental study on quality and safety of walnut oil during storage. There is present an argumentation of the factors that determine the walnut oil stability during storage. We analyzed different samples of oil obtained by cold pressing conditions (industrial and obtained under laboratory). Quality and oil stability depend on its chemical composition, especially the content of unsaturated fatty acids, as well as processing and storage conditions. During storage in walnut oil there were held various physicochemical and enzymatic changes that influence the quality. As quality indicators were used: peroxide value (PV), acid value (AV), enzyme activity, water activity, refractive index. There was a significant correlation between peroxide value, acid value and enzyme activity. Pearson correlation (R) has the following meanings: PV =f (AV) = 0.83; PV=f (APPO) = 0.96; AV=f(APPO) = 0.79. High Pearson correlation (R) PV=f (A PPO) = 0.9622 was found between VA and activities PPO. Perhaps the correlation between VP and the activity of other enzymes, including the lipoxygenases is even more significant.*

Key Words: walnut oil, Juglans regia L., unsaturated fatty acids, quality indicators, Pearson correlation

I. Introduction

Walnuts Juglans regia L. are known as relevant sources of oil beneficial to health. Although, walnut oil is not described by the current Committee on Fats and Oils of the Codex Alimentarius, small amounts are produced and commercialized in countries such as France, Spain, Chile and Argentina. The oil is used directly (without refining) for edible purposes, mainly as a salad dressing. It is also used in cosmetic industry as a component of anti wrinkle dry skin creams and anti-aging products [14].

Currently, nut orchards area in Moldova is 12,000 hectares, most of which are located in the central part of the country - in the districts Criuleni Noi, Ialoveni and Hincesti. Annually, about 80 percent of production is exported to 40 countries, including Italy, France, Germany, England etc. [29-31].
Average yield from one tree is 10-300 kg of nuts. The factors which determine large differences in crop walnut (Juglans regia L.) are covered in the study [28, 30]: climatic factors (light, temperature and air), edaphic factors (physicochemical properties of the soil, its degree of assurance with nutrients (microelements), water and air), organic factors and biotic factors. Of great importance in the walnut industry is harvesting fruits properly. Greater attention should be given to nuts harvested from the ground, as they may be at microbiological risk [24].

Insufficient scientific information on the quality of walnuts grown in Moldova and the composition of their oils necessitates carry out a systematic study of the most representative varieties of national production in order to contribute with scientific arguments and establish a major potential for walnut oil production at industrial level. Being rich in mono and polyunsaturated acids walnut oil is unstable during storage. It is important to know the factors which determine the quality of walnut oil.

II. Materials and methods

2.1. Plant material

Walnuts Juglans regia L. were collected manually in October 2011 in Chisinau, the center of Moldova. They were dried and stored at room temperature. From these nuts, by cold pressing, it was obtained walnut oil which served as research samples.

2.2. Served as a subject:

A - Industrial walnut oil, produced in Moldova;
B –Walnut oil, cold pressed (the laboratory screw press, Technical University of Moldova, Chisinau);
C - Walnut oil, cold pressed (B), without being decanted (separated).

For pressing there were used walnut varieties grown in Moldova. Oil samples were stored at 25-30^{o}C.

2.3. Analytical methods

The regress of lipid oxidation was assessed by measuring Peroxide Value (PV), free acidity (FA), Acid Value (AV), Activity Polifenoloxidase (APPO). For the Chemical analysis were used AOAC methods. Fats contents were determined by using AOAC 22.034.

Peroxide value represents the quantity of peroxide which is found in aliment and which has the capacity to liberate in one oxidative process iodine by potassium iodine [21].

For peroxide value, it was used the next formula:

$$PV = \frac{(V_1 - V_2) \times n}{g} \times 100 \text{, (meg/kg oil),} \quad (1)$$

where: V_1 = ml sodium thiosulphate used by sample titration;

V_2 = ml sodium thiosulphate used by reference sample titration;
g = quantity of sample, g;
n = solution normality.

The traditional method of determining PV, expressed in milliequivalents of active oxygen per kilogram of oil (meqO_2/kg), involves a titration of the oil contains potassium iodide in a chloroform-acetic acid mixture. The hydro peroxides oxidize the iodide to iodine, which can be determined by titration with sodium thiosulphate (AOAC official method 965,33).

Free acidity was determined by titration of the dissolved oil in a mixture of alcohol-ether (1:2) with an aqueous solution of sodium or potassium hydroxide (Standard EN ISO 660).

Acidity value represents KOH quantity in mg that is necessary for neutralization of free fat acids in one ml of fat (oil) [21].

AV was determined by the formula:

$$AV = \frac{28 \times V \times f}{m}; \text{ (mg KOH/g oil),} \quad (2)$$

where: V= solution volume of KOH used by titration (ml);

f = 0,8416, solution factor of KOH 0,5 N
m = sample quantity, in grams.

FA was determined by the formula:

$$FA = 0.5041 \times AV \text{, (g. oleic acid/100g oil)} \quad (3)$$

Polifenoloxidase Activity (APP) [23].

The principle to determine the polifenoloxidase is based on the determination of her property to oxidize pirocatehina to hinona, which oxidizes ascorbic acid at his turn.

Yeast extract from raw material was obtained as follows: 5g raw material was introduced into a 50 ml conical glass flask, stirring well. In 4 flasks were introduced 5 ml of filtrate and 10 ml of distilled water in each of them. Two flasks are heated and then boiled for 2 min to inactivate enzymes (control sample).

All 4 conical flasks cooled at a temperature of 20^{o}C. In each flask was introduced 5 ml of buffer solution with pH -6.8, 2 ml of pirocatehina solution and in the same sequence 5 ml of acid ascorbic solution. Conical flasks are shaken for 2 minutes since it is added ascorbic acid in the last one.

(5)

In the same sequence, in each sample, we added 1 ml of phosphoric acid, titrated it with iodine solution in the presence of starch. Because 1 ml of 0,02 N iodine solution is equivalent to 1,76 mg (10 micromoles) of ascorbic acid, polifenoloxidase activity compared to 1g of plant material, expressed in units of yeast is estimated according to the formula:

$$A_{ppo} = \frac{(V_0 - V_1) \times 10 \times 10}{5 \times 2} = (V_0 - V_1) \times 10 \ , \quad (4)$$

where: V_0 - volume of 0,02 N iodine solution (ml), used for titration of 5 ml control sample

V_1 - volume of 0,02 N iodine solution (ml), used for titration of work sample.

III. Results and discussion

Worldwide there are various studies aimed at oil stability during storage. In the conducted reference study it was found that the stability of walnut Juglans regia L. oil is determined by several factors such as: chemical composition of walnuts (oil), oil extraction method, packaging, storage parameters etc. The oil content in walnut kernel is determined by the genotype, but also may be influenced by environmental conditions and irrigation rate [22]. Minor differences were observed in crop year effects [16]. Oil content in different varieties of walnut Juglans regia L. reported in various studies it is between 570 … 710 g/kg [10-16]. The major components of walnut oil are triacylglycerols (TAGs; up to 980 g kg^{-1} oil), in which monounsaturated Fas (mainly oleic acid) and polyunsaturated FAS (PUFAS; linoleic and α-linolenic acids) are present in high amounts [7-10, 16-18, 22]. Nine TAG species have been characterized, trilinolein is the most abundant of them (≈37.7%), followed by dilinoleoyl-oleoyl-glycerol (18.5%) and dilinoleoyl-linolenoyl-glycerol (18.4%) [14]. The FA composition of walnut oil has been extensively reported to several cultivars from different geographic origins, including Argentina, [9, 20] the USA, [7] New Zealand, [1] Portugal, [19, 20] Turkey, [16, 17], Greece [26], and Germany [14] and Moldova [8].

The high content of unsaturated fats can lead to oxidative stability and reduced shelf life of walnut oil. Although walnut kernels contain a diverse array of phenolic and polyphenol compounds with strong antioxidant and radical-scavenging properties, only minor amounts could be present in the extracted oils. Protection against oxidative degradation seems to be limited mainly to tocopherol content. Other minor components characterized in walnut oil include phospholipids, sphingolipids, sterols (principally β-sitosterol), hydrocarbons (particularly C14 –C20 n-alkanes) and volatile components [1].

The majority of the volatile components found in walnut oil are products of oxidative breakdown of linoleic and linolenic acids forming hydro peroxides. Considering the sensory attributes characterizing such volatiles, they could adversely affect the sensory profile of the raw shelled walnut or its products (oil and flour) during handling and storage [6, 14].

The formation of some volatiles (pentanal, 2-heptenal and 2-octenal) can be better explained by an enzymatic pathway, rather than chemical (non-enzymatic) [14]. In walnuts Juglans regia L. may be present lipoxygenases enzyme (LOXs), which oxidases polyunsaturated fatty acids containing cis, cis-1,4-pentadiene fragments, such as linoleic and linolenic acids [11, 14]. The hydro peroxides produced by LOXs undergo splitting, form short and medium hydrocarbon chains (similar to those formed by non-enzymatic autoxidation) that contribute to the headspace volatile favors [20]. In Figure 1 it is present auto-oxidation scheme of linoleic acid from hydro peroxides to 9:13 position [25].

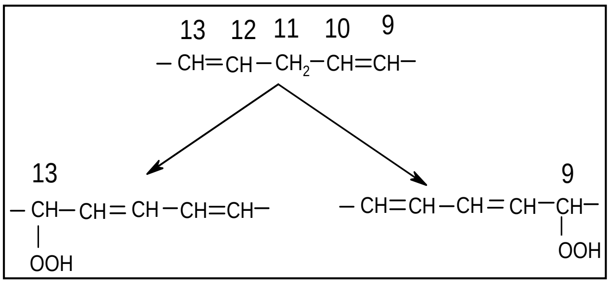

Figure 1. *Auto-oxidation scheme of linoleic acid form hydro peroxides to 9:13 position [26]*

In Figure 2 there are presents the autoxidation reactions of linoleic acid and formation of major volatile compounds in walnut oil [14].

The methods employed to extract lipids from oxidized foods may influence the obtained values from these oxidative products.

Oil extraction by pressing was not quantitative and therefore may not lead to a representative sample, particularly in the presence of polar compounds such as hydroperoxides [1, 9].

Degradation compounds that can be identified after the chemical, enzymatic oxidation and auto-oxidation of nut oil depend on walnut quality, oil extraction method and methods of evaluation.

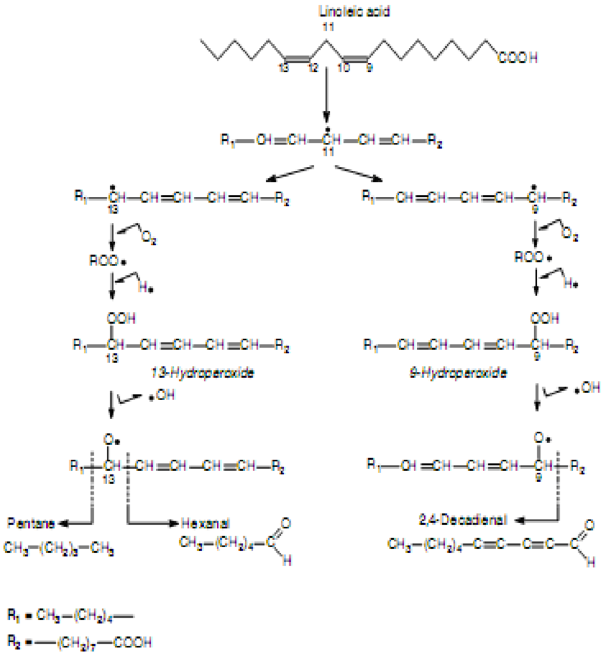

Figure 2. *Auto-oxidation reactions of linoleic acid and formation of major volatile compounds in walnut oil [14]*

The enzymatic oxidation differs from the auto-oxidation by following specificities: the reaction of the enzymatic oxidation of fatty acids occurs only in a diluted environment, such as an emulsion; the particularity of the catalytic activity of the enzyme lipoxygenase consists of the activity of the unsaturated fatty acids that contain only isolated double bonds; the speed of the oxidation depends mainly on pH and temperature [26].

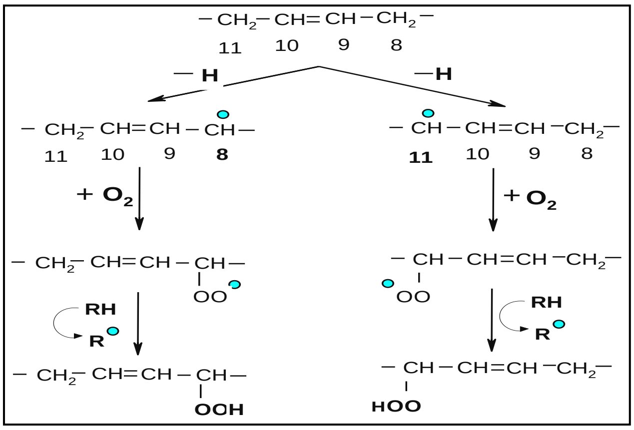

Figure 3. *Formation of hydro peroxides by autoxidation free oleic acid 8:11 positions [26]*

Figure 4 presents the General Scheme of enzymatic oxidation of lipids [26].

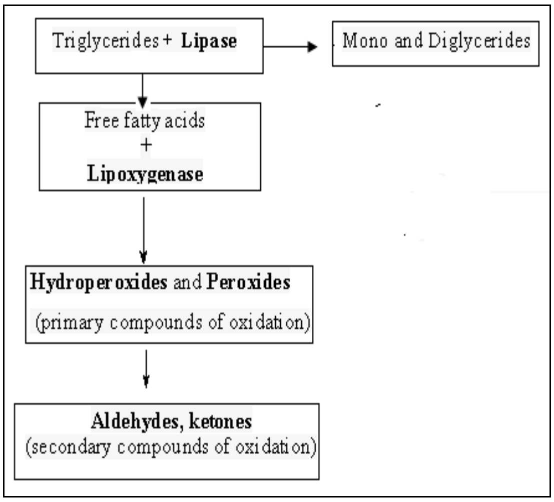

Figure 4. *General Scheme of enzymatic oxidation of lipids [26]*

Most of the groups of minor compounds are reported to have either a beneficial or detrimental effect on oil stability although the positive contribution of the primary antioxidants present in the unsaponifiable fraction is the major determinant in the resistance of virgin olive oil to oxidation [28].

Probably the same thing occurs in walnuts oil, because according to studies [13, 25], oil nuts also contain minor unsaponifiable compounds. This minor substances thrives enzymes in walnut oil.

Quality and safety of walnuts and walnut oil, during the storage, depend largely on the enzyme content and their activity. The study realized by M. Avramiuc (2011) presents interest. The purpose of this work was the lipase activity of sunflower seeds on its own substratum (sunflower oil), and on other substrata, belonging to seven plant species, searched under certain conditions of temperature and pH, was [3]. At pH 5, the highest enzyme activity was registered on soya been oil, followed, in order, by walnut, maize, peanut and sunflower oil (very close values for the last three ones). At pH 7.4, the greatest lipase activity value was registered on walnut oil, followed by peanut and maize oils. At pH 9.5, the highest lipase activities have been on sunflower oil, followed by walnut, pumpkin, soya bean and maize oils.

The lipolytic enzymes are hydrolases (lipases and phospholipases) and are involved into the lipids metabolism and demoting. Technologically, the lipolytic enzymes accomplish an uncontrolled fats hydrolysis, leading to food spoiling and to appearance of pronounced rancid taste and odor [5].

Figure 5 presents the enzymatic oxidation by lipases, hydrolases, phospholipases, liases, isomerases, dehydrogenases of unsaturated fatty acids [2, 4].

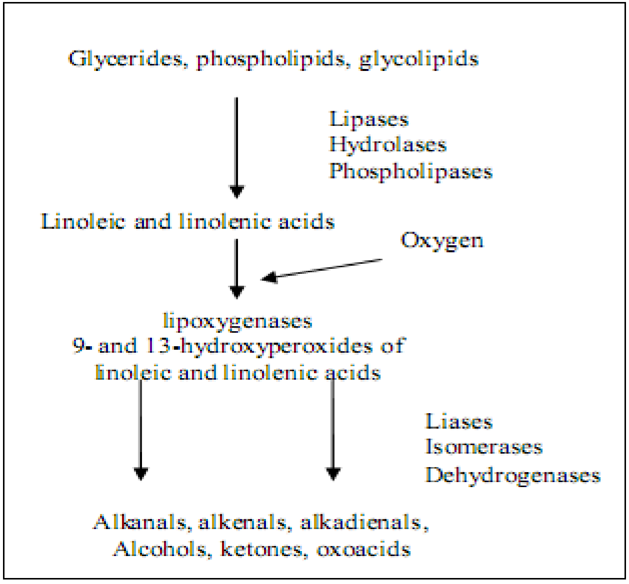

Figure 5. *Enzymatic oxidation of unsaturated fatty acids*

Table 1 includes the values of chemical and physical indicators Peroxide Value (PV), free acidity (FA), Acid Value (AV), Activity Polifenploxidase (APPO).

Table 1. *Change indicators PV, VA and A PPO in oils produced from different varieties of nuts grown in Moldova during storage*

Indicators tested	Term storage (days)	Samples tested		
		A	B	C
PV	0	-	8,0	9,5
	30	7.7	9,3	18,2
	60	10	12.6	24,5
	90	10	15,2	28,3
	120	11	28.1	35,6
VA	0	-	3.21	3,2
	30	3.30	3.36	4,7
	60	3.51	3,62	5,1
	90	3.73	3,74	5,7
	120	3.90	4,03	6,0
FA	0	-	1,62	1,61
	30	1.66	1,69	2,37
	60	1.77	1,82	2,57
	90	1.88	1,89	2,87
	120	1.97	2,03	3,03
APPO	0	-	0,75	1,5
	30	0.5	0,92	3,0
	60	0.6	1,0	3,7
	90	0.72	1,2	4,2
	120	1.0	1,5	4,3

PV- peroxide value, mg O2/kg oil, VA - acid value, FA - mg KOH/1g oil and g.oleic acid/100g oil APPO – activity polifenoloxidase, unit's activity.

A figure 6, 7 and 8 presents the correlation between the peroxide value (PV), acid value (AV) and activity PPO of walnuts oil. Pearson correlation was evaluated and tested between indicators.

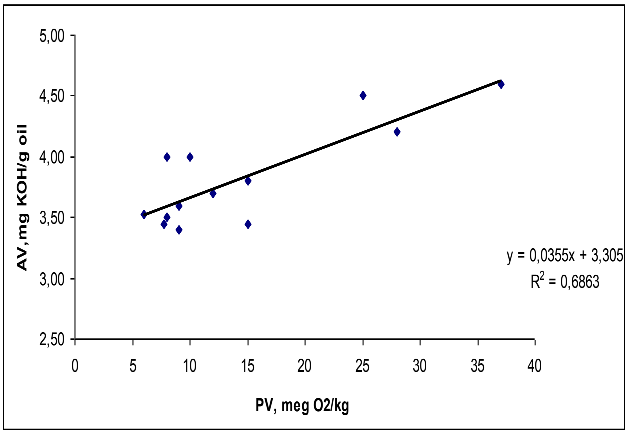

Figure 6. *Pearson correlations between peroxide value and acid value of walnuts oil. Pearson correlation: PV =f (AV) = 0,83*

High Pearson correlation (R (PV, A PPO) = 0,9622) was found between VA and activities PPO. Perhaps the correlation between VP and the activity of other enzymes, including the lipoxygenases is even more significant.

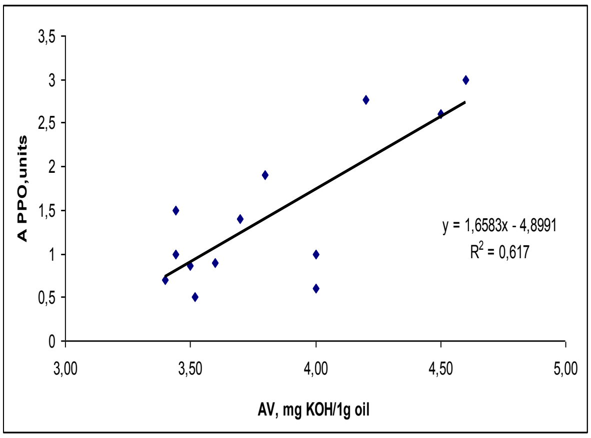

Figure 7. *Pearson correlations between activity PPO and acid value of walnuts oil Pearson correlation AV=f (APPO) = 0,79.*

It is necessary to study and appreciate the factors that cause oxidative and enzymatic processes in walnuts and walnut oil to extend the oil storage. The oxidative stability is an important parameter in ascertaining the quality of oils, as it gives a good estimation of their susceptibility to oxidative degradation.

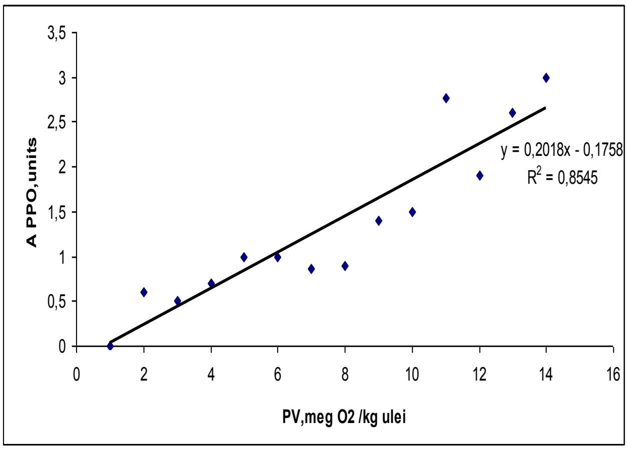

Figure 8. *Correlation between PPO activity and peroxide value.* Pearson correlation *PV=f (APPO) = 0,96*

IV. Conclusions

Walnuts Juglans regia L are important sources of vegetable proteins and polyunsaturated fatty acids. Nutmeg contains the optimum ratio of Ώ6 and Ώ3. Oxidative stability is an important criterion in ascertaining the quality of oils.

Quality and oil stability depends on its chemical composition, especially the content of unsaturated fatty acids, as well as processing and storage conditions.

During storage in walnut oil there are held various physicochemical and enzymatic changes that influence the quality.

There was a significant correlation between peroxide value, acid value and enzyme activity. Pearson correlation has the following meanings:

R (f = PV, AV) = 0,83; R (f = PV, A PPO) = 0,96; R (f = AV, APPO) = 0,79.

This paper presents a bibliographic and experimental study of enzymes' impact on quality of walnuts (Juglans regia L.) and walnut oil. Quality and safety of walnuts and walnut oil, during the storage, depend largely on the enzyme content and their activity. Enzyme activity in walnuts depends on storage conditions: temperature, humidity, *p*H, light access, packaging.

Sunlight increases enzyme activity. The core of walnuts should be stored in waterproof packaging to oxygen, water vapor, light, to avoid chemical and enzymatic degradation of walnuts and walnut oil.

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MOISTURE SORPTION CHARACTERISTICS OF A FLOURY MIX WITH ADDITION OF JERUSALEM ARTICHOKE FLOUR

A. G. Durakova, N. Toshkov, A. Yovchev

University of Food Technologies,
26, Maritza Blvd., 4002 Plovdiv, Bulgaria
e-mail: aldurakova@abv.bg

Absract. *Moisture equilibrium data (adsorption and desorption) of a floury mix prepared from type 500 flour and 5% Jerusalem artichoke flour were determined using the static gravimetric method of saturated salt solutions at three temperatures, 10, 25, and 40^{o}C. The range of water activities for each temperature was between 0.11 and 0.85. The equilibrium moisture content decreased with the increase in storage temperature at any given water activity. The experimental data were fitted to five mathematical models (modified Oswin, modified Halsey, modified Chung-Pfost, modified Henderson and Guggenheim-Anderson-de Boer). The monolayer moisture content was estimated using the Brunauer-Emmett-Teller equation.*

Key Words: sorption characteristics, Jerusalem artichoke flour /*Helianthus tuberosus* L./, floury mixes.

I. Introduction

Recent years have witnessed extensive work on the development of foods with natural products added to them in order to enrich the foods with biologically active substances for health-promoting diets. As a result, there is a growing necessity for the manufacture of flour mixes containing special flours, which aid various functions of the human organism [12].

Jerusalem artichokes possess the remarkable property consisting in perfect environment-bound self-defense. This plant does not take in nitrates, heavy metals or radioactive elements. In practice, its ecological purity does not depend on the conditions of the environment and the products, which contain it as an ingredient, assume valuable functional and prophylactic properties. The biologically active substances in Jerusalem artichokes are of great importance to the physiology of human beings [1].

At an international conference in Russia in 2004, Jerusalem artichokes (*Helianthus tuberosus* L.) were declared to be “the bioenergetic crop of the 21st century”, a unique plant.

The flour from Jerusalem artichoke tubers contains up to 20% of dry matter, including up to 80% of polymer homologs of fructose, inulin. Inulin is a polysaccharide whose hydrolysis leads to the production of a sugar that is harmless to diabetics – fructose [2]. Jerusalem artichokes are high in cellulose and ash, as follows (mg % per dry matter): iron – 10.1; manganese – 44.0; calcium – 78.8; magnesium – 31.7; potassium – 1382.5; sodium – 17.2 [3].

The sorption characteristics (equilibrium and monomolecular moisture content) enable us to properly determine the processing regimes and techniques, the storage and packaging of the product [4].

The interdependence between equilibrium moisture content *(M)* and water activity (a_W) is provided by a sorption isotherm, which is experimentally constructed at specific temperatures.

Monomolecular moisture can be regarded as a critical point of the sorption isotherm and its variation bears important consequences for products that are to be stored.

The conditions, such as temperature and relative air humidity, under which the product has monomolecular moisture may be considered to be optimal for its storage.

The research on the subject recommends a great number of models describing the interdependence between equilibrium moisture content (EMC) and water activity (a_W) [15]. The modified Chung-Pfost, Henderson, Halsey and Oswin, which take into account the effect of the temperature, have been recommended by Chen and Morey [9]. These models have been adapted to suit food products as standard isotherm-describing equations by the American Society of Agricultural Engineers (ASAE) [5].

II. Materials and methods

2.1. Material

The focus of this study is a floury mix containning type 500 wheat flour and 5% of Jerusalem artichoke flour. The type 500 wheat flour was produced by “Zagore” JSC, town of Stara Zagora. Jerusalem artichokes were supplied in the form of thin, dried to 6.2% moisture discs by “Charodejtsi-07” SP, town of Parvomaj. Experimental milling was carried out with 0.5-kg samples and continued until the particle size of 200 µm was reached. In order to determine fats (0.46%), proteins (7.58 d.b.), carbohydrates (74.8%), ash (0.29% d.b.) and initial moisture (13.5% d.m.), standard AOAC procedures were applied (1990) [6].

2.2. Methods

The EMC of the floury mix - from type 500 flour and 5% Jerusalem artichoke flour - was determined at 10, 25 and 40° C. The static gravimetric method was applied [7, 17]. For the adsorption process, the flour was dehydrated in a desiccator with $CaCl_2$ at a room temperature for 20 days prior to the beginning of the experiment. The desorption isotherms were determined on samples hydrated in a glass jar over distilled water at a room temperature to approximately 30% d.b. moisture content. Samples of 1 ± 0.02 g were weighed in weighing bottles. The weighing bottles were then put in hygrostats with six saturated salt solutions (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, NaCl, KCl) used to obtain constant water activity environments Tab.1 [7]. All of the used salts were of reagent grade. At high water activities ($a_w>0.70$) crystalline thymol was placed in the hygrostats to prevent microbial spoilage of the flour. The hygrostats were kept in thermostats at 10, 25 and 40 ± 0.2ºC. Samples were weighed (balance sensitivity ±0,0001g) every three days. Equilibrium was ascertained when three consecutive weight measurements showed a difference less than 0.001 g. The moisture content of each sample was determined by the oven method (105ºC for 24 h) in triplicates.

Table. 1. *Constant water activities of salts at all three working temperatures*

Salt	10°C	25°C	40°C
LiCl	0,113	0,113	0,112
CH_3COOK	0,234	0,225	0,201
$MgCl_2$	0,335	0,328	0,316
K_2CO_3	0,431	0,432	0,432
NaBr	0,622	0,576	0,532
NaCl	0,757	0,753	0,747
KCl	0,868	0,843	0,823

2.3. Analysis of data

The following models were used to verify the description of the sorption isotherms [7]:

Modified Chung-Pfost

$$a_w = \exp\left[\frac{-A}{t+B}\exp(-CM)\right] \tag{1}$$

Modified Halsey

$$a_w = \exp\left[\frac{-\exp(A+Bt)}{M^C}\right] \tag{2}$$

Modified Oswin

$$M = (A+Bt)\left(\frac{a_w}{1-a_w}\right)^C \tag{3}$$

Modified Henderson

$$1-a_w = \exp\left[-A(t+B)M^C\right] \tag{4}$$

GAB

$$M = \frac{AB'C'a_w}{(1-B'a_w)(1-B'a_w+B'C'a_w)} \tag{5}$$

where:

M is the average moisture content, % d.b.;

a_w is the water activity, decimal;

A, B and C are coefficients;

t is the temperature, ºC.

In the GAB model, coefficients B′ and C′ are presented in the form:

$$B' = B\exp\left(\frac{h_1}{RT}\right) \tag{6}$$

$$C' = C\exp\left(\frac{h_2}{RT}\right) \tag{7}$$

A nonlinear, least squares regression program was used to fit the four models to the experimental data (all replications). The suitability of the equations was evaluated and compared using the mean relative error *P* (%); the standard error of moisture (SEM) and the randomness of residuals e_i [9]:

$$P = \frac{100}{N}\sum\left|\frac{M_i - \hat{M}_i}{M_i}\right| \tag{8}$$

$$SEM = \sqrt{\frac{\sum\left(M_i - \hat{M}_i\right)^2}{df}} \tag{9}$$

$$e_i = M_i - \hat{M}_i \tag{10}$$

where:

M_i and $\hat{M}_i$ are experimentally observed and predicted by the model value of the equilibrium moisture content;

N is the number of data points;

A, B and C are coefficients.

df is the number of degree of freedom (number of data points minus number of constants in the model).

The monolayer moisture content (MMC) for each temperature is calculated by using the Brunauer-Emmett-Teller (BET) equation and the experimental data for water activities up to 0.45 [13]:

$$M = \frac{M_e C a_w}{(1 - a_w)(1 - a_w + C a_w)} \qquad (11)$$

where:

M_e is the MMC, % d.b.;

a_w is the water activity, decimal;

C is the coefficient.

III. Results and discussion

The obtained mean values of EMC, based on triplicate measurements for the respective water activity and temperature, are presented in Table 2 for adsorption and in Table 3 for desorption.

The EMC values increase with an increase in the temperature at constant a_w. The effect on this type of flour is also manifested in other food products, which contain high amount of sugars. The reason for this is the decomposition of sugars after which the flour starts absorbing larger quantities of water. The same effect also applies to the processes of adsorption and desorption. Similar trends for many foods have reported in the literature [4].

Table. 2. *Equilibrium moisture content EMC (% d.b.) of flour mix by adsorption at different water activities a_w and temperatures t (°C)*

Salt		10°C			25 °C			40 °C	
	a_W	EMC^a	sd	a_W	EMC^a	sd	a_W	EMC^a	sd
LiCl	0,113	9,38	0,08	0,113	7,2	0,11	0,112	6,81	0,31
CH_3COOK	0,234	12,01	0,26	0,225	10,78	0,18	0,201	8,57	0,16
$MgCl_2$	0,335	13,16	0,08	0,328	12,11	0,13	0,316	10,22	0,39
K_2CO_3	0,431	14,81	0,04	0,432	12,6	0,26	0,432	11,89	0,17
NaBr	0,622	17,38	0,2	0,576	14,37	0,13	0,532	13,23	0,09
NaCl	0,757	19,93	0,15	0,753	17,46	0,08	0,747	17,21	0,12
KCl	0,867	25,49	0,61	0,843	21,91	0,24	0,823	18,38	0,57

[a] mean value of triplicates

Table. 3. *Equilibrium moisture content EMC (% d.b.) of flour mix by adsorption at different water activities a_w and temperatures t (°C)*

Salt		10 °C			25 °C			40 °C	
	a_W	EMC^a	sd	a_W	EMC^a	sd	a_W	EMC^a	sd
LiCl	0,113	8,85	0,25	0,113	7,08	0,42	0,112	7,14	0,35
CH_3COOK	0,234	12,77	0,08	0,225	9,29	0,19	0,201	8,97	0,22
$MgCl_2$	0,335	13,97	0,09	0,328	10,99	0,09	0,316	10,29	0,39
K_2CO_3	0,431	-	-	0,432	-	-	0,432	-	-
NaBr	0,622	17,17	0,01	0,576	14,38	0,11	0,532	13,43	0,03
NaCl	0,757	20,46	0,44	0,753	18,55	0,08	0,747	18,36	0,47
KCl	0,867	24,85	0,13	0,843	20,96	0,3	0,823	24,43	0,13

[a] mean value of triplicates

Fig. 1 gives the experimental data obtained after adsorption and desorption at 10ºC. The sorption isotherms have an S-shape profile [8]. The hysteresis effect is statistically significant, at a level of significance α=0.05, in the water activity range 0,1÷0,9.

The coefficients for the three-parameter modified models, *P* and *SEM* values are presented in Table 4 for adsorption and Table 5 for desorption**.** The coefficients of *P* and *SEM* values for the GAB model are given in Table 6.

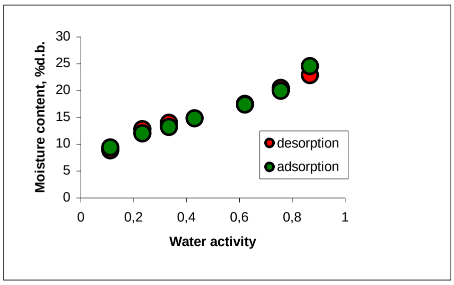

Fig. 1. *Comparison of sorption isotherms at 10 °C*

Table. 4. *Model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for adsorption*

Model	A	B	C	*P*	*SEM*	Residues	*R*
Chung-Pfost	584,0567	29,554	0,196392	**3,28**	**0,69**	**Random**	**0,991**
Oswin	16,1474	-0,087264	0,249126	4,10	0,63	Non-random	0,991
Halsey	7,723056	-0,017753	2,94853	5,56	0,81	Non-random	0,983
Henderson	0,000148	13,45288	1,901835	17,17	2,44	Non-random	0,858

Table. 5. *Model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for desorption*

Model	A	B	C	*P*	*SEM*	Residues	*R*
Chung-Pfost	965,6956	85,45513	0,178618	**4,71**	**1,21**	**Random**	**0,981**
Oswin	14,66454	-0,024846	0,27353	6,31	1,31	Non-random	0,976
Halsey	6,742091	-0,004011	2,69707	6,98	1,39	Non-random	0,968
Henderson	0,00068	30,5717	2,000064	61,04	10,84	Non-random	0,915

Table. 6. *Coefficients (A, B, C, h_1, h_2), mean relative error (P, %), and standard error of moisture (SEM) of GAB model*

Process	*A*	*B*	*C*	h_1	h_2	*P*	*SEM*	*R*
Adsorption	11,3858	0,053423	21,75131	5786802	499247,6	15,61	3,52	0,98508
Desorption	10,03749	0,534796	26,98197	524379,3	359107,6	5,73	1.39	0,97514

The results show that the lowest *P* and *SEM* values were obtained with the Chung-Pfost model. The graphical analysis of the residues demonstrates that the distribution is random for model, which means that the model is suitable for the description of flour mix (from type 500 flour and 5% Jerusalem artichoke flour).

To calculate the BET monolayer moisture content, the model (11) is linearly transformed:

$$\frac{a_w}{(1-a_w)M} = P + Qa_w \ . \qquad (12)$$

The linearization of the experimental data for $a_w < 0.5$ in adsorption and desorption is shown in Fig. 2 and Fig. 3, respectively.

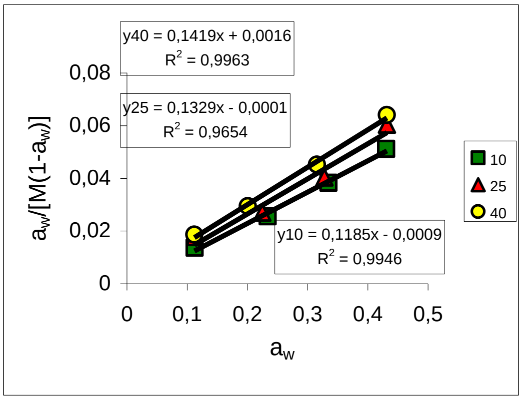

Fig. 2. *Linearization of the BET model for the three temperatures in adsorption*

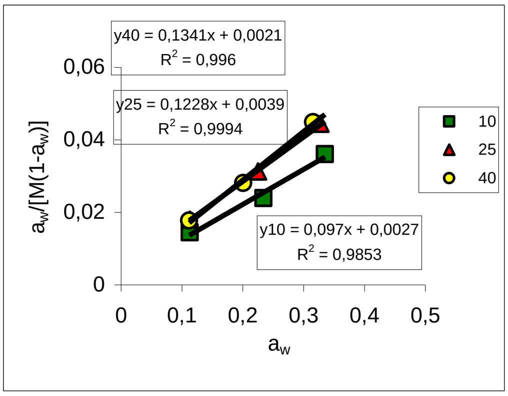

Fig. 3. *Linearization of the BET model for the three temperatures in desorption*

On the basis of the coefficients of the linear equation, the MMC for the respective temperature is calculated and the results are presented in Table 7.

Table. 7. *BET monolayer moisture content MMC (% d.b.) of flour mix at several temperatures*

t (°C)	Ads.	Des.
10	8,5	10,03
25	7,53	7,89
40	6,97	7,34

The results demonstrate that with adsorption the increase in temperature is accompanied by a decrease in MMC, whereas with desorption the temperature has an insignificant effect on MMC.

The monolayer moisture content is a critical point of the sorption isotherm. If the moisture content value of a product is getting lower than the value of the MMC, an oxidation of the unsaturated lipids is commencing [10, 11, 14].

We think that the following conditions – temperatures of 10, 15 and 40^{o}C and relative air humidity of 0,1 – 0,4 – at which the product has monomolecular moisture in the 6,97 – 10,03 % d.b. range, can be considered to be optimal for a long period of storage.

IV. Conclusions

The experimental research on a floury mix containing type 500 flour and 5% Jerusalem artichoke flour demonstrated that:

1. The sorption capacity and the monolayer moisture content of flour mix - from type 500 flour and 5% Jerusalem artichoke flour decreased with an increase in temperature at constant water activity.
2. At temperatures of 10, 25 and 40^{o}C, the equilibrium isotherms were experimentally obtained.
3. The modified Chung-Pfost model is suitable for describing the relationship between the equilibrium moisture content, the water activity and the temperature for the floury mix - from type 500 flour and 5% Jerusalem artichoke flour.
4. The monolayer moisture content ranged within 6.97 ÷ 10.03% d.b.
5. Temperatures of 10, 25 and 40^{o}C as well as relative air humidity within 0.1 – 0.4, when the product has monomolecular moisture in the 6.97 - 10.03 % d.b. range, can be considered to be optimal for a long period of storage.

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INVESTIGATION OF SOME LOCAL BULGARIAN CULINARY SPICES. 2. COSTMARY (*Chrysanthemum balsamita* L.*)*

T. N. Sapundzhieva, M. R. Baeva, P. A. Merdzhanov,
A. T. Popova, I. N. Alexieva, A. S. Stoyanova

University of Food Technologies, Plovdiv, 26, Maritza Blvd., 4002, Bulgaria

Abstract. *The chemical composition of essential oil from the leaves of costmary (Chrysanthemum balsamita L.) obtained by water distillation was analyzed using GC/MS. 40 compounds were identified and the main (above 3 %) were carvone (47,81 %), α-thujone (12,56 %), germacrene B (5,23 %), benzaldehyde (4,64 %) ethylbenzene (3,96 %) and germacrene D (3,13 %). The antibacterial activity of obtained from the leaves of costmary cytosol was teste against Gram-positive and Gram-negative pathogenic bacteria.*

Keywords: *Chrysanthemum balsamita* L.; *Asteraceae*; essential oil, cytosol.

I. Introduction

Many species have been recognized to have medicinal properties and beneficial impact on health, e.g. antioxidant activity, digestive stimulation action, antiinflammatory, antimicrobial, hypolipidemic, antimutagenic effects and anticarcinogenic potential. Crude cytosols of herbs and spices, and other plant materials rich in phenolics are of increasing interest in the food industry because they retard oxidative degradation of lipids and thereby improve the quality and nutritional value of food [1, 11, 13, 14, 15].

Spices and essential oils are used by the food industry as natural agents for extending the shelf life of foods. Essential oils in plants generally are mixtures of several components. Some of those presence exert antimicrobial effects such as components in oregano, clove, cinnamon, citral, garlic, coriander, rosemary, parsley, lemongrass, sage and vanillin. They exert direct or indirect effects to extend foodstuff shelf life or as antimicrobial agent against a variety of Gram – positive and Gram-negative bacteria [2, 5, 9, 11].

Costmary (*Chrysanthemum balsamita* L.) is a medicinal plant from family *Asteraceae*. It is native to Mediterrenean region and today is cultivated in many countries.

The plant and its preparations (infusion, and decoction) are used as herbal tea, flavoring agent in foods and in folk medicinal as hepatoprotective, antibacterial, sedative, cardiotonic and carminative resources.

The plant has different phytochemical compounds, for example essential oil [4, 6, 7] with major volatile constituents camphor (about 50 %), carvone (40 - 50 %) and α-thujone (20 - 25 %) and sesquiterpene lactones [12]. Four hemotypes have been recorded – carvone, camphor, camphor-thujone and carvone-α-thujone [4].

In the flora of Bulgaria the leaves from costmary used in folk medicine and in cuisine. It is no data on the use of its essential oil and cytosols in food products.

The aim of the study is to determine chemical composition of essential oil and inhibition activity of cytosol against some pathogenic bacteria.

II. Material and methods

The leaves of costmary (*Chrysanthemum balsamita* L) were harvested at the beginning of blossom in 2011 in the vicinity of the town Plovdiv, Bulgarian.

The moisture of the fresh raw (91,5 %) estimated by drying to 105 ^{O}C, according to Russian Pharmacopoeia [8].

The oil content was determined in laboratory glass apparatus of British Pharmacopoeia modified by Balinova and Diakov [3] for 2 h and the yield is estimated on the basis of absolutely dry matter.

The oil obtained was dried over anhydrous sodium sulfate and stored in tightly closed dark vials at 4 ^{O}C until analysis.

Gas Chromatography Analysis: GC analysis was performed using gas chromatograph Agilent 7890A; column HP – 5 ms (30 m x 250 μm x 0,25 μm); temperature - 35 ^{O}C/3 min, 5 ^{O}C/min to 250 ^{O}C for 3 min, total 49 min; carrier gas helium 1ml/min constant speed; split ratio 5:1

GC/MS analysis was carried out on a massspectrometer Agilent 5975C, carrier gas helium, the temperature and the column are the same as the GC analysis.

The identification of chemical compounds is made by comparison to their relative retention time and library data. The identified components are arranged in order to the retention time and quantity in percentage.

Microbial analysis: Antibacterial activity is tested against Gram-positive bacteria - *Listeria monocytogenes* NCTC 11994 and *Staphylococcus aureus* ATCC 25093, and Gram-negative bacteria - *Escherichia coli* ATCC 8739 and *Salmonella enterica subsp. Enterica serovar Abony* NCTC 6017.

The media are inoculated with 24-hour suspension of the corresponding bacteria (cell concentration 10^6 CFU/ml).

For the microbial analyses it was obtained cytosol under aseptic surroundings by mashing fresh leaves, and decanting cytosol after preliminary washing of leaves under tap water, washing under sterilized distilled water and soaking one hour in 70 % ethanol for eliminating the epiphytic microflora.

A modified method of Tagg and McGiven [10] is applied for measuring the zone of the pathogen's growth inhibition around metal rings (Ø 6 mm), with placed within 0,12 ml of cytosol.

All experiments were done in triplicate and the results were statistically evaluated.

III. Results and discussions

The content of essential was 0,28 % and the yield was low. The difference from the reported in literature are probably due to the climatic conditions in the respective locality in which the plant is growing.

The oil was light yellow and had a sharp odor.

The chemical composition of the oil shown (Table 1) that 40 components (98,29 % of the total composition), 15 of which above 1 % and 30 - below 1 %. The main compounds (above 3 %) were: carvone (47,81 %), α-thujone (12,56 %), germacrene B (5,23 %), benzaldehyde (4,64 %) ethylbenzene (3,96 %) and germacrene D (3,13 %).

Comparison of the volatile constituents of our oil and the reported data shows that there are some qualitative and quantitative differences between the environmental conditions of different plant origin.

In conclusion, this study demonstrates the occurrence of carvone hemotype of Bulgarian costmary essential oil.

Table 1. *Chemical composition of essential oil from leaves of costmary*

№	Name	RI	%
1.	Ethylbenzene	854	3,96
2.	α-Pinene	938	0,09
3.	Camphene	954	0,08
4.	Benzaldehyde	962	4,64
5.	Sabinene	971	0,55
6.	β-Pinene	979	0,07
7.	Decane	1000	0,10
8.	p-Cymene	1025	0,07
9.	D-Limonene	1028	2,54
10.	Eucalyptol	1031	1,31
11.	γ-Terpinene	1058	0,08
12.	α-Thujone	1104	12,56
13.	trans-p-Mentha-2,8-dienol	1099	1,73
14.	Trans- 2-Cyclohexen-1-ol, 1methyl-4-(1-methylethenyl)	1139	0,12
15.	Pinocarveol, trans-(-)-	1145	0,09
16.	cis-Verbenol	1153	0,07
17.	Pinocarvone	1165	0,08
18.	(-)-Terpinen-4-ol	1177	0,06
19.	Cyclohexanol, 2-methylene-5-(1-methylethenyl)-	1188	0,79
20.	α-Terpineol	1190	0,07
21.	Dihydrocarvone	1195	0,89
22.	cis-2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)	1205	0,41
23.	(-)-Carvone	1254	47,81
24.	trans-Chrysanthenyl acetate	1276	0,84
25.	(-)-Bornyl acetate	1288	0,07
26.	Tridecane	1300	0,06
27.	cis-Carvyl acetate	1332	0,10
28.	trans-Carveyl acetate	1346	0,62
29.	α-Copaene	1387	0,08
30.	Germacrene D	1475	3,13
31.	β-Bisabolene	1510	1,73
32.	δ-Cadinene	1514	0,65
33.	α-Patchoulene	1518	0,11
34.	Germacrene B	1560	5,23
35.	Germacrene D-4-ol	1570	0,08
36.	Cubenol	1580	0,70
37.	α-Cadinol	1640	2,37
38.	α-Muurolol	1649	1,33
39.	Apiol	1680	1,57
40.	Farnesol	1725	1,45

Figure 1 shows the classes of identified compounds, based on functional groups in the volatile oil.

The total oxygenated terpenes constituted the highest percentage of the components of the essential oil constituting 87,84 %. The oil consisted on oxygenated terpenes (73,5 %), hydrocarbon terpenes (14,6 %), aromatic hydrocarbons (5,7 %), aromatic oxygenated (4,7 %) and other components (1,5 %).

The essential oil of costmary is currently used in medicine, and several other industries such as food, perfumery and confectionery [6, 7].

The cytosol of costmary was light green and had a specific odor.

In table 2 are presented the size of zones, preventing from growth the pathogenic bacteria around the metal rings.

In the present study, among the four bacteria tested, *Listeria monocytogenes* was the most sensitive to the cytosol of costmary, while *Escherichia coli* and *Salmonella enterica* was the most resistant.

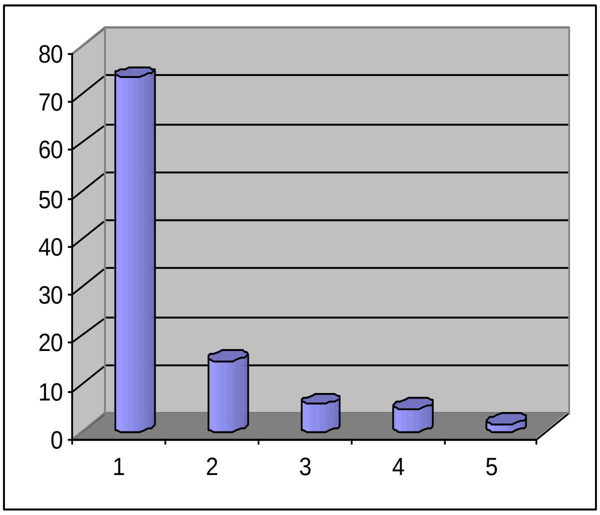

Figure 1.*Aromatic compounds in oil from leaves of costmary, %.*
1 – oxygenated terpenes, 2 hydrocarbon – terpenes;, 3 – aromatic hydrocarbons, 4 – aromatic oxygenated, 5 – others.

Phenolic compounds are probably the major constituents responsible for antimicrobial activity of costmary cytosol [7, 9].

These results are similar to the published on the susceptibility of Gram-negative and Gram-positive bacteria to antibacterial agents [11].

Table 2. *Inhibition zones from cytosol from leaves of costmary*

Inhi bitor	Diameter of the zones (mm), prevented from growth of bacteria:			
	L. monocytogenes	*S. aureus*	*E. coli*	*S. enterica*
costmary	30	20	10	12

IV. Conclusion

The chemical composition of essential oil from leaves of costmary (*Chrysanthemum balsamita* L.) and antimicrobial activity of cytosol is reason to their application in culinary products or natural cosmetic and medicine purposes.

Acknowledgements

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STEROL COMPOSITION OF COTTONSEED OILS FROM BULGARIAN VARIETIES OF COOTON

M. Perifanova- Nemska

University of Food Technology, Plovdiv, 26, Maritza Blvd., 4002, Bulgaria

Abstract: *The total content of sterols in oils of Bulgarian varieties of cotton seeds has been investigated. No difference of sterols content is observed. The ratio free and esterified sterols to the total sterols has been established. The main part of sterols in investigated cottonseed oils is in free condition - 79.3 to 83.3 %. In the fraction of free sterols the main component is ß-sitosterol (89.3-92.8 %). By esterified sterols (sterolesters) ß-sitosterol is also observed in the biggest content 84.8 – 85.6 %, but it is less than in the free sterols. In the investigated oils from Bulgarian varieties beside ß-sitosterol, campesterol, stigmasterol, Δ^5 avenasterol were observed cholesterol, brasicasterol, Δ^7 stigma and Δ^7 avenasterol*

I. Introduction

Vegetable oils are one of the richest sources of sterols. Sterols, which are part of the unsapunificated substances have a biologically activity.

Sterol composition is important indicator of the quality of vegetable oils because of the requirement to provide information about the content of cholesterol in foods. In the oil sterols are as in free (71-91%) as well as esters of high fatty acids [2, 12].

The total content of sterols (free and esterified) in oils is from 0,27 to 1 %. The β-sitosterol is the main agent - above 50 %.

Cottonseed oil contents around 0,26 – 0,64 % total sterols [1, 4, 10, 11, 12]. Sterol fractions depend of geneses, climate and geographical growing conditions and the difference can be significant. The total sterol content increased with rising of the temperature of the environment. In the same time, according to Piironen at all, raises the content of campesterol and decrieses the β-sitosterol content. According to literature in cottonseed oils are identify cholesterol, bracicasterol, stigmasterol (1,0 – 6,8 %), Δ^5 avenasterol (1,8-7,3 %), Δ^7-stigmasterol (up to 1,4 %), Δ^7–avenasterol (0,5-3,3 %).

In the literature there is information about total sterol content and their individual composition, but no data about individual composition of separate fractions - free sterols and sterol esters of cottonseed oils, derived from Bulgarian varieties cotton.

The aim of the article is to investigate content and composition of sterol fractions in oils from *new Bulgarian varieties cotton*.

II. Materials and methods

Materials

Fruit material. The varieties of cottonseeds, for deriving of the investigated oils, has been provided from the Institute of cotton in Chirpan. The investigations has been carried out for six varieties, selected in the last 10 Years: Chirpan-539, Beli Iskar 800,

ML 240, Avangard 264, Perla-267 and Vega-412. Sort Chirtpan, one of earlier selected, is used as a standard.

Methods

The oil from seeds is extracted in laboratory conditions in Soxhlet apparatus with hexane for 8 h. After rotation vacuum distillation of the solvent the extracted oils were weighted (3).

Sterols: The total sample (sample size of 100 mg, precisely measured) was applied on 20 cm x 20 cm glass plates (ca. 1 mm thick silica gel G layer) and developed with hexane-acetone, 100:8 (by volume). Free (Rf=0.4) and esterified sterols (Rf=0.8) were detected under UV light by spraying the edges of each plate with 2′,7′-dichlorofluorescein, they were then scraped, transferred to small glass columns and eluted with diethyl ether. The solvent was evaporated under a stream of nitrogen and the residue was weighed in small glass container to a constant weight. Free sterols were then subjected to gas chromatography (GC, without derivatization). Sterols esters were hydrolyzed with ethanolic KOH (7), sterols were extracted with light petroleum ether and purified by TLC under the above conditions prior the GC analysis. Sterol composition was determined on HP

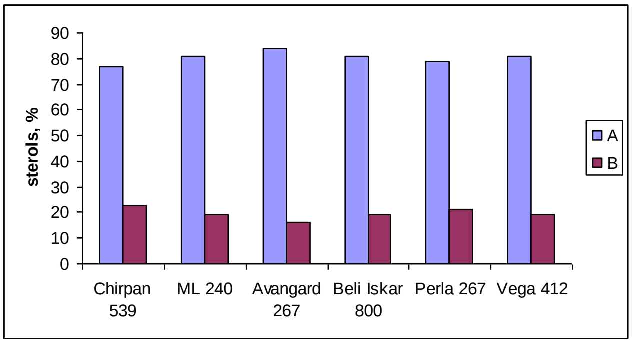
5890 gas chromatograph (Hewlett Packard GmbH, Austria) equipped with 25 m x 0.25 mm HP5 capillary column (Agilent Technologies, Santa Clara CA, USA) and flame ionization detector. Temperature gradient from 90 °C (held for 2 min) to 290 °C at 15 °C /min then to 310 °C at 4 °C /min and held at this temperature for 10 min; the injector temperature was 300 °C and the detector temperature was 320 °C. Nitrogen was the carrier gas at a flow rate 0,8 mL/min; split 100:1. Identification was confirmed by comparison of retention times with those of a standard mixture of sterols (5).

III. Results and discussion

The data about total content of sterols (free and esterified) in investigated samples are presented in Table. 1 and has been found to be 0.26 - 0.32 %. A significant difference between investigated oils is not found. This value is close to the content of sterols in other cottonseeds oils (1, 4, 8, 12).

The ratio free and esterified sterols to total sterols has been established and the results are on figure 1. It shows that the main part of sterols in investigated cottonseed oils is in free condition - 79.3 to 83.3 %. The rest part is in esterified form.

In the fraction of free sterols the main component is ß-sitosterol (89.3-92.8 %), followed by campesterol (3.9 – 4.8 %) and stigmasterol (0.6 – 3.0 %).



A – free sterols; B – sterol esters

Figure 1. *Ratio free and esterified to total sterols*

By esterified sterols (sterolesters) ß-sitosterol is also observed in the biggest content 84,8 – 85,6 %, but it is less than in the free sterols. Δ^5 avenasterol (5,0 – 5,3 %) and campesterol (4,0 – 5,0 %) are followed. In sterol esters the content of Δ^7 avenasterol (1,1 – 1,6 %) is also higher then this in free sterols (0,2 – 0,4 %).

Compared with literature dates for cotton seed oils some differences are observed [4, 6, 12]. In the investigated oils from Bulgarian varieties beside ß-sitosterol, campesterol, stigmasterol, Δ^5 avenasterol were observed cholesterol, brasicasterol, Δ^7 stigma and Δ^7 avenasterol.

Higher is the content of cholesterol in sterol esters. This can be explain with separated stages by biosynthesis of different lipids classes. The cholesterol is synthesized on the first stage of biosynthesis in the plants, when the biosynthesis of esters of fatty acids goes. In this way the main part of cholesterol associates with fatty acids in esters [9].

IV. Conclusion

1. ß-sitosterol content is predominant in the oils, derived from Bulgarian cotton seed varieties, as in fraction of total as well in fraction of free and esterified sterols.
2. In the individual composition of sterol of the three fractions significant difference is not found.
3. In the investigated oils from Bulgarian varieties beside ß-sitosterol, campesterol, stigmasterol, Δ^5 avenasterol were observed cholesterol, brasicasterol, Δ^7 stigma and Δ^7 avenasterol.

Table 2. *Individual composition of free, esterified and total Sterols of Bulgarian cottonseed oils*

Sort sterols,%	Chirpan 539			ML240			Avangard 267			Beli Iskar 800			Perla 267a267			Vega 412		
	free	esterified	total	free	Esterified	total	free	esterified	total	free	esterified	total	free	esterified	total	free	esterified	total
cholesterol	0,2	1,4	1,4	0,3	1,3	0,4	0,5	1,3	0,4	0,3	1,6	0,4	0,3	1,6	0,5	0,2	1,5	0,4
brasicasterol	0.2	0,4	0,4	0,3	0,2	0,4	0,3	0,5	0,3	0,4	0,4	0,2	0,4	0,5	0,3	0,3	0,6	0,4
stigmasterol	0,7	1,0	1,6	1	0,9	2,4	2,9	1	2,3	3	0,9	2,7	0,7	0,7	2,7	0,6	0,8	2,6
ß-sitosterol	92,6	85,4	91,4	92,1	85,4	88,9	89,3	85,6	90,2	89,3	85,3	92,2	92,8	84,8	89,2	92,6	85,3	90,2
campesterol	4	4.1	3,9	3,9	4,9	4,5	4,8	4,7	3,8	4,3	4,4	4,2	3,9	5	3,8	4	4,7	3,3
Δ5 avenasterol	0,8	5,1	1,5	0,7	5,3	1,8	0,6	5,1	2	0,7	5	2	0,9	5,3	2,3	0,7	5	1,9
Δ7 stigmasterol	1,2	1	0,9	1,4	0,9	1,1	1,4	0,6	1,3	1,3	1	1	1,6	0,6	0,9	1,2	0,7	0,8
Δ7 avenasterol	0,3	1,6	0,4	0,3	1,1	0,5	0,2	1,2	0,6	0,3	1,3	0,8	0,3	1,5	0,3	0,4	1,4	0,4

* values obtained for each indicator are averaged, averaged deviation (SD) is determinated and uncertainty is in ranges от ±0.1до ±0.9 by α=0.05

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APPLICATION OF INFORMATION TECHNOLOGY ASSESSMENT OF ENERGY SAVINGS IN INDUSTRY

N. Hr. Bozukov

University of Food Technologies
26, Maritza Blvd., 4002 Plovdiv, Bulgaria

Abstract: *The report describes the algorithm of the program that was developed to determine the assessment of energy savings in the manufacture of a product in the industry. Amount of energy saved in one year is calculated by a formula specified in methodology. The evaluation of the energy savings in industry is done by measuring and/or estimating consumption before and after the implementation of the energy efficiency measure.*

The data and methods are based on measurements and estimates. In assessing the measure of energy efficiency we can not rely on specific measurements and therefore distinguish between methods of measurement and evaluation methods of energy savings.

Key words: energy savings in industry, program algorithm

I. Introduction

Sites industry is one of the largest consumers of energy, because they are integrated systems of buildings and production – a technological process for products or services realization. To achieve energy efficiency in industry sites optimal production is required – a technological process with certain quality at minimal energy consumption. The industry can reduce energy costs by using energy management industry.

Objects in the industry are major users and consume significant amounts of energy from the total energy needs of the country. Reducing energy consumption for industrial purposes can be achieved by using new technologies. Energy efficiency may be achieved by applying intelligent power management and using renewable energy sources. This power will be independent, flexible, adaptive, energy saving.

II. Aspects in the evaluation of energy savings

The data availability and the ability of recovery is essential for precise and accurate assessment of energy savings in methodologies for energy efficiency. It is important to be provided most accurate information and a set of necessary data before any assessment . It should be borne in mind that the evaluation of energy service or measure energy efficiency is usually not possible to rely on specific measurements.

It is necessary to distinguish between methods for measuring energy savings and methods estimating energy savings, the latter are more common and are associated with much lower costs.

Energy audit is to determine the level of energy consumption to identify opportunities to reduce it and to recommend measures to improve energy efficiency [7]. Methods have developed that aim to demonstrate the implementation of individual measures or groups of measures to improve energy efficiency in various sectors of economic and social life [6].

Energy savings in industry are determined by measuring and / or estimating consumption before and after the implementation of the energy efficiency measure. The amount of the saved energy is equal to the difference between the energy used before the introduction of the measure or program to improve energy efficiency and use of energy, measured after administration.

The developed methods include the following directions [6]:

- Replacement of equipment with energy efficient one. In this direction the baseline is the specific energy consumption of existing equipment before replacement, if there is evidence of this. In the event of no evidence that consumption as a baseline can be used for data average specific energy consumption of similar existing equipment.

- Updating equipment or building. The baseline in this direction is the specific energy consumption before the modernization of equipment or building. If there are no specific data on the consumption of the equipment average consumption of such existing equipment can be used for data . In the absence of specific energy consumption of the building prior to the implementation of energy saving measures the baseline can be used for specific consumption of buildings built according to the design standards for the year of construction of the building.

- Acquisition of energy-efficient equipment or building. In this direction the baseline is the specific energy consumption of older equipment before replacement. In the absence of baseline data average specific energy consumption of new equipment sold in the country as the base year, or the rules for the energy performance of buildings existing in the base year are considered.

III. Description and implementation of algorithms for energy savings

An algorithm to calculate the estimate of the energy savings in the industry has been developed. This algorithm is described with a block - and the scheme is implemented in two versions. Programming language system for scientific and engineering calculations is used in the first option MatLab [1, 2].

MatLab is open, flexible and easily adaptable to the solution of a task assigned by the user. It is based on a matrix representation of the data. It is used in many fields of knowledge, because it contains tools including data processing, operations on matrices, vectors, polynomials, complex numbers, signal analysis, digital filtering, two-dimensional and three-dimensional graphics and other [3, 8].

MatLab supports arrays with more than two dimensions. Multidimensional arrays can be numeric, character, cell, or structure arrays. Multidimensional arrays can be used to represent multivariate data. MatLab provides a number of functions that directly support multidimensional arrays.

MatLab structures are array-oriented data constructs. They provide a convenient way to group related data of different types [8].

Structures are MatLab data constructs with named "data containers" called fields. The fields of a structure can contain any kind of data.

In MatLab, one function take another as a parameter. This feature serves a wide variety of purposes.

The second option is used spreadsheet MS Excel (fig. 2).

The algorithm of the program to process the data on energy savings in the industry described in block diagram (fig. 1).

Input:

SECIc - specific energy consumption for the production of the unit before applying energy saving measures kWh / unit / year;

SECIн - specific energy consumption for the production unit after implementing energy saving measures kWh / unit / year;

W - output during the year (t, m2, number, etc.)

Calculates and displays the amount of saved energy to produce a product in the industry for one year FES measures kWh / year.

If the program runs again, it goes to start, if not running, its execution is completed.

After starting the program, run the steps in its algorithm. Methodology is used for energy savings in the industry. After performing all the tasks on the program it displays the final result, representing savings of energy to manufacture a product in the industry for one year by the following formula:

$$FES = \left(SECI_C - SEC_H\right) * W, kWh/year \quad (1)$$

The entire session working with the program, all variables and data used in the program are stored in a separate file that can be opened, viewed and printed.

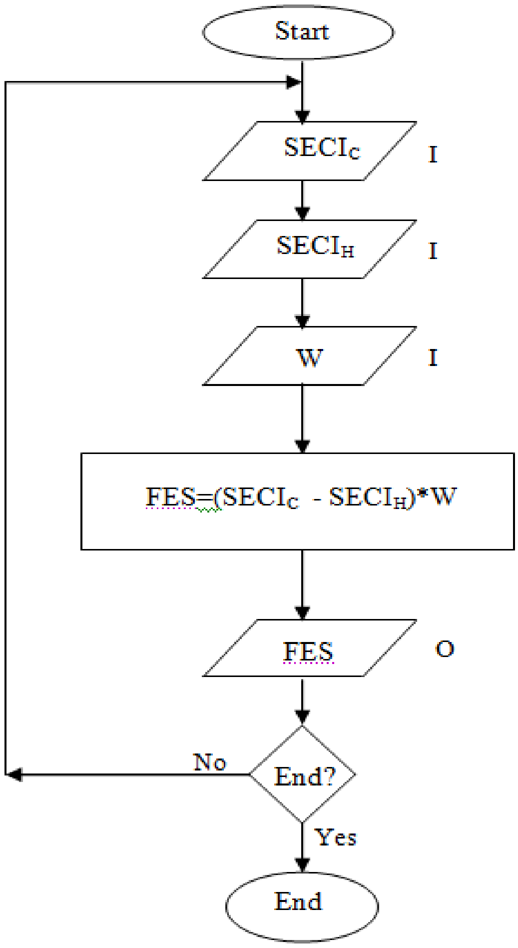


Figure 1. *Block - diagram of energy saving program in the industry: I - Input, O – Output*

IV. Use a spreadsheet to evaluate the energy savings in industry

MS Excel spreadsheet is used for input, processing and output of interrelated data when performing calculations using formulas and functions, data visualization graphs, charts, etc. [7].

The main advantage of spreadsheets is the ability to calculate the numerical data with formulas. It is user configurable to make such uses or proposed program built-in functions. Where the information formulas or functions are automatically recalculated.

Each table can be formed in different ways depending on its intended use.

The spreadsheet offers a graphical representation of data (with charts) and helps to quickly and easily analyze and forecast processes and phenomena.

The program algorithm is used to process data on energy savings in the industry described in block diagram (fig. 1).

In cell L5 table input (fig. 2):

$SECI_c$ - specific energy consumption for the production of the unit before applying energy saving measures kWh / unit / year;

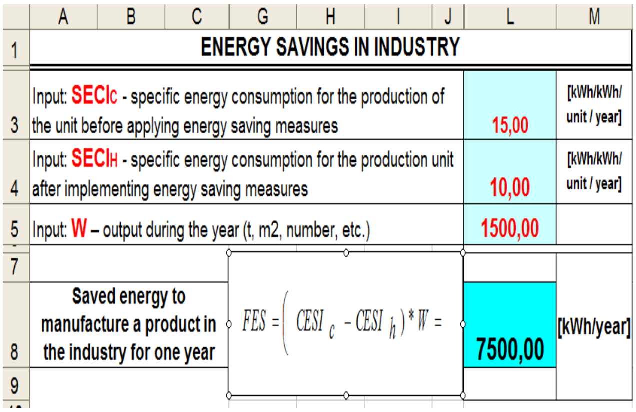
In cell L6 table is introduced:

$SECI_{н}$ - specific energy consumption for the production unit after implementing energy saving measures kWh / unit / year;

W - output during the year (t, m^2, number, etc.);

Calculated and displayed in cell L7 table, saved energy to manufacture a product in the industry for one year FES [kWh / year].

With MS Excel spreadsheet is easy to input data and calculated results, necessary for the implementation of a methodology that aims to demonstrate the implementation of individual measures or groups of measures to improve energy savings in the industry.



	A	B	C	G	H	I	J	L	M
1	ENERGY SAVINGS IN INDUSTRY								
3	Input: **SECIc** - specific energy consumption for the production of the unit before applying energy saving measures							15,00	[kWh/kWh/ unit / year]
4	Input: **SECIн** - specific energy consumption for the production unit after implementing energy saving measures							10,00	[kWh/kWh/ unit / year]
5	Input: **W** – output during the year (t, m2, number, etc.)							1500,00	
7									
8	Saved energy to manufacture a product in the industry for one year			$FES = \left(CESI_c - CESI_h \right) * W =$				7500,00	[kWh/year]
9									

Figure 2. *Implementation of algorithms for energy savings in the industry in a spreadsheet*

V. Advantages of the algorithm for evaluation of energy savings

Information technology assessment of energy savings and its algorithm have advantages and disadvantages. Some of the advantages are:

- in the accumulation of sufficient data base the real impact of energy savings in the industry can be assessed very accurately;
- using the database a complete analysis can be made and the planned project and the achieved energy performance in the real operation can be compared
- certificate issued within the period provided by law for energy efficiency would have a solid justification of factual data.
- it is easy to handle and calculate the data required for the application of the methodology, which aims to demonstrate the implementation of individual measures or groups of measures to improve energy savings in the industry with information technology.

VI. Conclusion

Information technology, data processing, evaluation and calculation of energy savings is a good and convenient way to control and give objective analysis of the impact of the application of energy efficiency measures in industry. In applying such information technology for calculating the energy savings in the industry high reliability, easy transfer and data processing can be achieved.

The availability of data and the possibility of collecting and processing them is essential for accurate and fair assessment of the energy savings in the developed methodologies. It is important to have most accurate information and data before any assessment.

Information technology should be used in each of the methodologies for energy savings. Energy saving systems are focused on efficient energy use through innovative technologies. Due to modern industry it combines flexibility, functionality, aesthetics, environmental and energy efficiency.

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INFORMATION TECHNOLOGY FOR SAVINGS FROM DECENTRALIZATION OF COMPRESSOR STATIONS

N. Hr. Bozukov

University of Food Technologies
26, Maritza Blvd., 4002 Plovdiv, Bulgaria

Abstract: *With the passage of centralized compressor station to the local production of compressed air to achieve a number of economic effects. The report describes the information technology to calculate the savings from decentralization and payment of a compressor station. Information technology is good, convenient and reliable means of control and objective analysis. The algorithm is described with a block - scheme. The program was developed using the programming language of the system for scientific and engineering calculations MATLAB.*

Key words: information technology for calculating savings from decentralization of compressor

I. Introduction

Food industry uses compressed air in technological processes for the production of various products for business establishments. There are compressor stations for production of compressed air and air conductors for transportation. Application of new technologies in modern companies reduces the need of compressed air energy and compressor stations become uneconomical. The use of local compressors with smaller facilities located close to users appears to be propriate.

II. Economic effect

Decentralization of compressor stations with a move to local production of compressed air leads to economic effect:

- Reduction of power consumption for production due to the decommissioning of energy reciprocating compressors and off substations;
- Liquidation of long trunk lines for compressed air and off losses in transit;
- Dividing users of compressed air required pressure levels and maintenance of the level of actual consumption;
- Reducing power consumption shutdown of wasteful stations;
- Reduction in operating losses for breach of diagnosis and the need for space heating central compressor stations.

III. Algorithm for calculating the savings from decentralization and payment of compressor station

The determination of annual energy consumption in the production of compressed air from a central compressor station is done with the following formula (1):

$$E_C = P_y * K_u * T_c, \quad kWh/year \qquad (1)$$

- P_y - total established power groups electric - equipment (compressors, power supply substation plant drying air cooling compressors), KW [2];
- K_u - coefficient use of electric power of electric - equipment is determined by the technology of manufacturing process [2];
- T_c - the annual number of hours of use of electricity - average equipment load is determined by the technology of manufacturing process [2];

The determination of the annual energy consumption while ensuring the needs of the production of compressed air with local compressors are made by the following formula (2):

$$\sum_{I=1}^{n} E_{LI} = P_{yI} * K_{uI} * T_{cI}, kWh/year \qquad (2)$$

EL1, ..., ELn - an annual energy consumption of every local compressor, which is determined by formula (3):

$$E_{LI} = P_{yI} * K_{uI} * T_{cI}, \quad kWh/year \qquad (3)$$

- P_{yI} - established power compressor kW;
- K_{uI} - coefficient use of electrical power;
- T_{cI} – annual number of hours of electricity use - equipped with medium load.

The determination of energy savings from reducing losses off the main pipelines, compressed air supply and implementation of an automatic adjustment of the performance of the new compressor, which is about 12% of the E_C, is done with the following formula (4):

$$E_T = 0{,}12 * E_C \ , \quad kWh/\,year \quad (4)$$

The determination of energy savings from measures implemented is done with the following formula (5):

$$dE \ = E_C + E_T - E_L \ , \quad kWh/\,year \quad (5)$$

Determining the fuel economy of decentralization compressor station with the installation of compressors local reporting losses in the grid for electricity supply to the entrance of consumer is done with the following formula:

$$dB \ = dE \ * \left(1 + k_p\right) * B_E * 10^{-6}, Tsf \quad (6)$$

- B_E - specific fuel consumption for electricity generation, which is assumed to be equal to the actual fuel stations closing energy system for years preceding calculations, Ysf/kWh;
- K_p - coefficient of losses in electric networks for electricity, with a mean of 0.105.

The definition of capital is done using the formula (7):

- Type of compressor local elected as the need for production of compressed air and pressure.
- Preliminary value of local compressor is determined by the bids of manufacturers;
- The value of the dismantling work is determined by the company that made them;
- The value of the project - innovatory work is 5-10% of the value of the equipment;
- The value of construction works is determined by the company that made them.

$$k = C_{ob} + \left(0{,}05 \div 0{,}1\right) * C_{ob} + C_{dem}, + C_{snp} \quad (7)$$

The determination of the period for payment shall be made by the following formula (8):

$$C_{pok} = k * \left(dB * C_{gop}\right) \quad (8)$$

- k - capital, thousands levs;
- dB - fuel economy by implementing specific cost per tonne;
- C_{gor} – value of one ton limit fuel, thousand levs.

Before each measurement is important to provide as accurate information as a set of necessary data.

IV. Description and implementation of the algorithm and program for calculating savings from decentralization and payment of compressor station

Developed an algorithm to calculate the savings from decentralization and payment of a compressor station. This algorithm is described with a block - scheme is implemented with the programming language system for scientific and engineering calculations MatLab [1, 3].

MatLab is based on a matrix representation of the data. Contains tools, including data processing, operations on matrices, vectors, polynomials, complex numbers, signal analysis, digital filtering, two-dimensional and three-dimensional graphics and other [7, 8]. It is used in various fields of science and technology. MatLab is open, flexible and easy to apply to the solution of a specific task.

The sequence of steps of the algorithm is:

Input:

- P_y - total established power groups electric - equipment (compressors, power supply substation plant drying air cooling compressors), KW;
- K_u - coefficient use of electric power of electric - equipment is determined by the technology of manufacturing process;
- T_c - the annual number of hours of use of electricity - average equipment load is determined by the technology of manufacturing process;

Calculates and displays the annual energy consumption in the production of compressed air from a central compressor station in formula (1).

Input:

- E_{L1}, … E_{Ln} - annual energy consumption of every local compressor, which is determined by formula (3), where:
- P_{yI} - established a local power compressor, kW;
- K_{uI} - coefficient use of electrical power;
- T_{cI} - the annual number of hours of use of electrical equipment of each compressor with an average load.

Calculates and displays the annual cost of electricity in ensuring the needs of the production of compressed air compressors local by formula (2).

Calculates and displays energy savings from reducing losses off the main pipelines, compressed air supply and implementation of an automatic adjustment of the performance of the new compressor, which is about 12% of the E_C, the formula (4).

Calculates and displays energy savings from implemented actions by formula (5). Input:

- B_E - specific fuel consumption for electricity generation, which is assumed to be equal to the fuel stations closing energy system in the year preceding calculations, Ysf / kWh;

- K_p - coefficient of losses in electric networks for electricity, with a mean of 0,105.

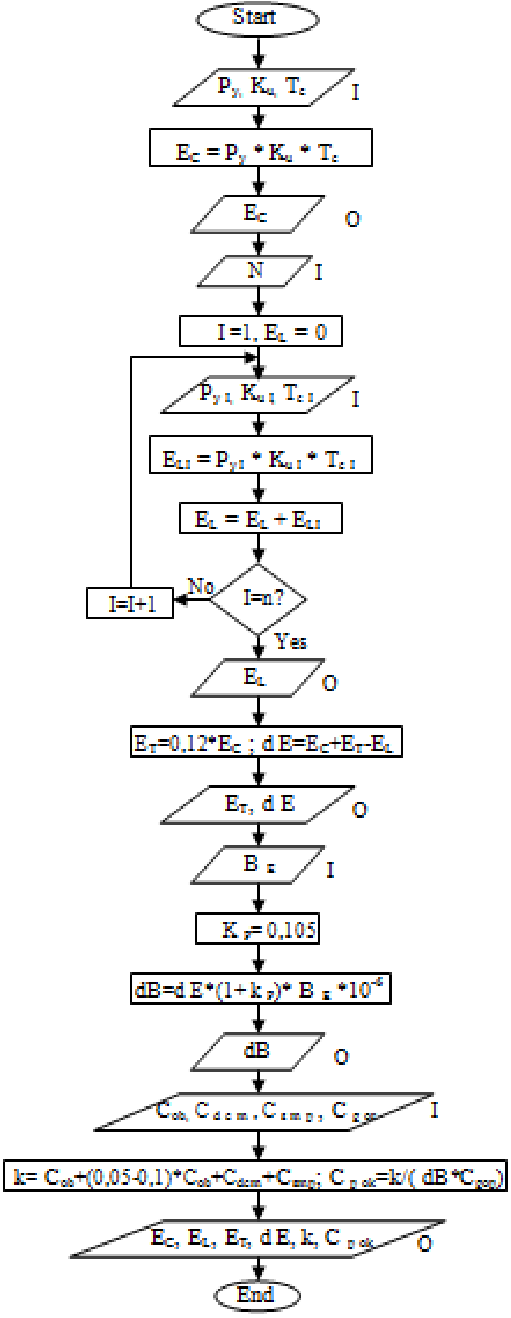

Fig. 1. *Block - diagram of the program to calculate the savings from decentralization and paying compressor station: I-input, O-output*

Calculate and display fuel economy of decentralization compressor station with the installation of compressors local reporting losses in the set in the supply of electricity to consumers at the entrance of the formula (6). Input:

- The value of the equipment C_{ob};

- The value of the dismantling work C_{dem};

- The value of construction C_{smp}.

The value of the project - innovatory work is 5-10% of the value of the equipment;

Calculates and displays the value of investments by formula (7). Input:

- C_{gor} - value of one ton limit fuel (thousand Levs).

Calculated and displayed in the payout formula (8).

After starting the program, the steps in its algorithm are run. After completion of the work with the program the results of calculating the savings from decentralization and paying compressor station are shown : E_c, E_L, E_T, dE, k, C_{pok}

The entire working session of the program, all variables and data used in the program are stored in a separate file that can be opened, viewed and printed.

V. Advantages of the algorithm and evaluation program of energy savings

Information technology assessment of energy savings has the following advantages:

- easily and quickly processed data and calculated results needed to calculate the savings from decentralization and paying compressor station;

- in the accumulation of sufficient data base can assess the real impact of the decentralization of compressor station very precisely ;

- using the database a complete analysis can be done and the planned project and the savings achieved in actual operation can be compared.

VI. Conclusion

Information technology is a good, convenient and reliable means of control and objective analysis for calculation the savings decentralization of compressor station.

The availability of data and the possibility of collecting and processing is essential for accurate and fair assessment of the savings. It is important to have most accurate information and data before any assessment.

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WAYS TO REDUCE DOSING ERROR OF GRANULAR PRODUCTS IN LINEAR WEIGHT DOSING MACHINES

O. Gavva, A. Derenivska, L. Krivoplyas-Volodina

Faculty of Mechanical Engineering and Packaging Equipment,
National University of Food Technologies, Kiev, Ukraine

Abstract. *In this article there is the result of laboratory research of linear weight dosing machine, providing permanent product flow through outlet port of hopper and minimizing the dynamic part of granular product dosing error, by rational placing of weighing container.*

Key words. granular product; linear weight dosing machine; dosing accuracy; dynamic dosing error; weighing container.

I. Introduction

Granular products have the great part of all food products. They are different by structure and mechanical properties and packing of such kind of products are providing in different container types. These factors define the structure of packing machine.

Now days, linear weight dosing machines are dominating on the market. This is due to price, dosing accuracy and productivity ratio. It is totally understandable that more accurate and productive machine do exist, but there problem is the price. So the main priority is given to upgrades and development of linear weight dosing machines.

In general view the structure of linear weight dosing machines for granular products may be described as a complex of different elements, any of each performs it's function. (fig. 1). Granular products permanently or periodically are supplied to receiving hopper 1, from witch by the use of feeder 2 it goes to container 3 where the dose is forming. Weight of the product, in the container 3, are measured by weight sensor 4 and controlled by handling system 5. Handling system 5 of a modern packing equipment includes PLC and analog-digital transducer.

When the weight of the product in the container gets near to the dose value, handling system 6 turns transportation system 2 and regulated shutter 7, in hopper 1, to slow feeding control position and when the dose value are achieved, it stops the transportation system.

The modification of dosing machine provides research of it's characteristics based on integrated approach to designing. Metrological characteristics and ways to improve the accuracy, productivity for specified granular product are evaluated. Main criteria of the research are the dosing accuracy. It is important to know the factors and there interrelation which have influence on the dosing accuracy.

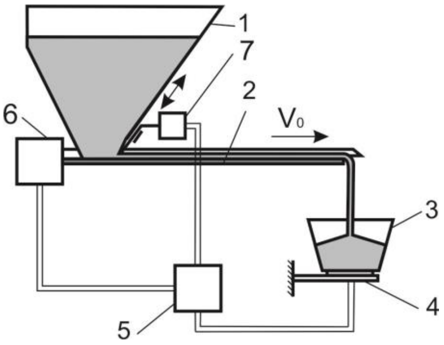


Figure 1. *Structure scheme of linear weight dosing machine for granular products.*

Dosing error depends from machine productivity, its structure, scheme, and design concept of machine parts. In the scientific work [1] there are three types of errors (three sources of dosing error):

drift – characterized by startup mode of machine. Minimal value are achieved by the delays interdiction between startup and beginning of dosing

static – characterized by performance inaccuracy of weighing system elements or else. This part of error is less than one percent.

dynamic – caused by transient in strain gauge transducer in time off the production flow to the container. Minimal value are achieved by time delays (installing of the filters witch define average weight value). It reduces the productivity of dosing machine.

Dynamic error consists from two parts: modeline and own. Modeline error depends from product feed intensity, cross-sections of the feeder feed channel area or else. Own error are defined by special characteristics of granulated product and it's interaction with machine elements. Reduce it by constructive changes is almost impossible. That is why the main regulated part of dosing error is modeline error.

Irregularity of granulated product feed in linear weight dosing machine – main source of modeline part of dynamic dosing error. It does not depend from the feeder type and product which are dosing. Modeline error depends from feeding speed, pressure of the product in hopper on working element of the feeder, cross-section of feeder channel area, using of special stabilizers of production height, time of product second feed, else.

To minimize one part of modeline error it is necessary to provide stable speed of product going through hopper outlet channel. For automatic regulation of hopper shutter position it's recommended to use a pneumatic positioning actuator (fig. 2) which consists of: controller, electropneumatic proportional pressure regulator, microcontroller of linear positioning actuator [2]. According to product level in the hopper, the position of the shutter is changing by the fact of inlet pressure value change in pneumatic actuator. Also, to minimize modeline part of dynamic dosing error, it is necessary to provide a correct placing of the weighing container against working element of the feeder.

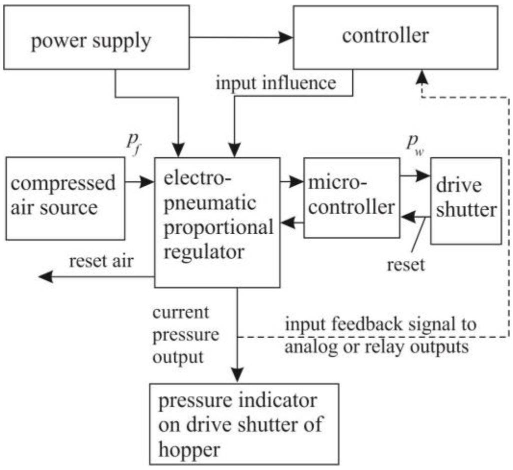


Figure 2. *Pneumatic positioning actuator of the hopper shutter control, structure scheme:* p_f *– feed pressure;* p_w *– working pressure*

Research methods: used methods of mathematical modeling.

II. Results and discussion

To define the rational working parameters of the feeder and to place weighing container the next assumptions will be adopted: granular products - disconnected; small fractions. It is possible to ignore the particles size and consider the granular product as a continuous medium. The movement of the product can be described by using laws of hydraulics.

To define rational cinematic and dynamic parameters of shutter movement by pneumatic positioning actuator, depending from product movement from the hopper intensity, the mathematic model are created. Total power load on the shutter are displayed on fig. 3.

Actuated shutter equation [3,4]**:**

$$M \cdot (d^2 x) / (dt^2) = p_1 \cdot F_1 - p_2 \cdot F_2 - F_{m1} - F_{m2} - \ldots$$

$$\ldots - F_{m3} - F_{m4}\,. \qquad (1)$$

Inlet chamber pressure change equation:

$$dp_1 / dt = \{k \cdot f_{L1} \cdot (R_g \cdot T_M \cdot (p_M^2 - p_1^2)^{0.5} / [F_1 \cdot (x + \ldots$$

$$\ldots + x_{01}) \cdot (\xi_1)^{0.5}]\} - \{k \cdot p_1 \cdot dx / [(x + x_{01})dt]\}. \qquad (2)$$

Rod chamber pressure change equation:

$$dp_2 / dt = \{k \cdot f_{L2} \cdot (R_g \cdot T_2 \cdot (p_2^2 - p_a^2)^{0.5} / [F_2 \cdot (S - x + \ldots$$

$$\ldots + x_{02}) \cdot (\xi_2)^{0.5}]\} - \{k \cdot p_2 \cdot dx / [(S - x + x_{02}) \cdot dt]\}, \qquad (3)$$

where: M – reduced mass of the shutter moving parts and positioning actuator; x – current value of the actuator rod movement; t – movement time of the rod; p_1, p_2 – pressure in rod and piston chambers; p_a – atmosphere pressure; F_1 – cross-section area of the piston, F_2 – useful area of the piston; k – granular product movement factor; f_{L1} – cross-section area of the inlet tube; f_{L2} – cross-section area of the outlet tube; T_2 – air temperature, that exhaust; T_M – system air temperature; R_g = 287 – specific gas constant, S – working stroke of the rod; x_{01}, x_{02}– *begin/end coordinate of the piston*; ξ_1, ξ_2 – inlet tube resistance coefficient.

Sliding friction forces:

- Product - shutter:

$$F_{m1} = f_1 \cdot F_n; \qquad (4)$$

- Shutter - guide:

$$F_{m2} = f_2 \cdot (F_n + m \cdot g), \qquad (5)$$

where m – shutter mass;

- Piston – positioning pneumatic actuator:

$$F_{m3} = f_3 \cdot F_n \;; \qquad (6)$$

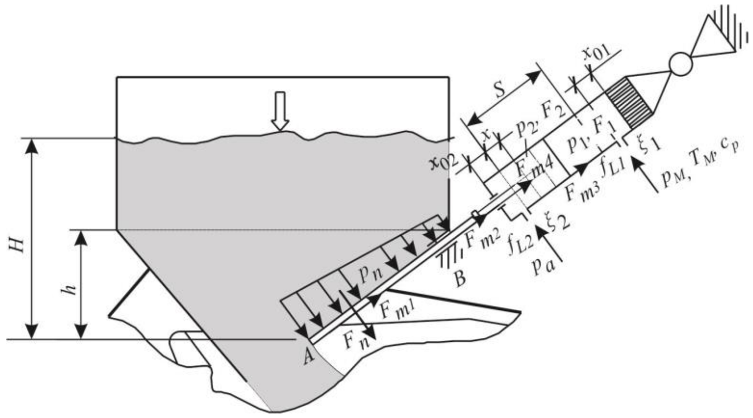


Figure 3. *Generalized shutter load force counting scheme depending on hopper production affect.*

- Positioning actuator rod:

$$F_{m4} = f_4 \cdot F_n \;; \qquad (7)$$

where: f_1, f_2, f_3, f_4 – sliding friction coefficient respectively to above values; F_n – the resultant force power of the product on the shutter, it's equal to:

$$F_n = 0{,}5 \cdot (\cos^2\alpha + k \cdot \sin^2\alpha) \cdot \gamma \cdot S \times \ldots$$

$$\ldots \times l \cdot b \cdot (H + h), \qquad (8)$$

where: k – granular product movement coefficient; α – hopper shutter slope angel; γ – specific product weight; l – shutter working part length; b – shutter width; H, h –product level height upper the shutter in A and B points.

Mathematics dependences counting results (1...8), which describes shutter movement in the hopper by the use of pneumatic actuator, are viewed in graphs on fig.4 considering such input values: *production – millet;* $\gamma = 800$ kg/m^3; $b = 0{,}1$ m; $S = 0{,}05$ m; $h = 0{,}380$ m; $H = 0{,}790$ m; $M = 1$ kg; $p_a = 1$ bar; ; $p_m = 6$ bar; $F_1 = 2{,}011 \cdot 10^{-4}$ m^2; $F_2 = 1{,}728 \cdot 10^{-4}$ m^2; $f_{L1} = f_{L2} = 1{,}963 \cdot 10^{-5}$ m^2; $T_M = 290$ K; $S = 0{,}050$ m; $x_{01} = x_{02} = 0{,}05$ m.

To realize any constant shutter movement law it's necessary to change f_{L1} and f_{L2} respecting the functional dependence. This functional solution enables the intensity regulation of the product feeding from the hopper.

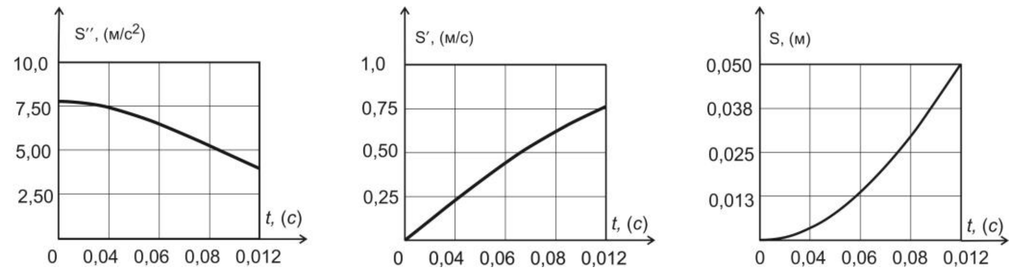
Definition of the weighing container rational placing are made with the condition, that the feeder is performed as a vibrator or belt conveyer (fig. 5).

In the dose forming process the weight sensor are forced by constant masses, and variable mass of the product, which is feeding to weighing container [5].

Total force on the weight sensor F_Σ defines by the sum of static and dynamic force (fig. 5):

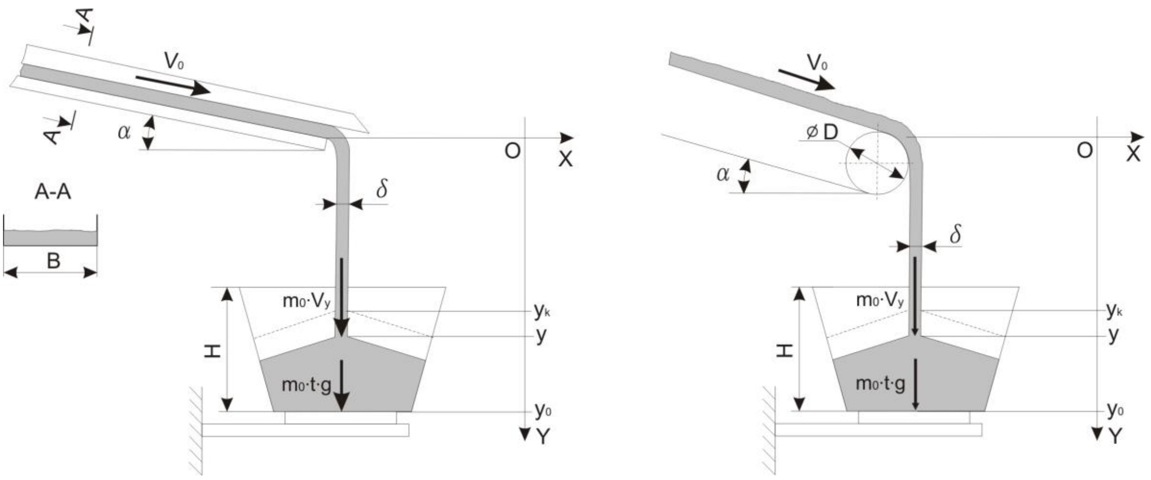
$$F_\Sigma = F_s + F_d\,, \qquad (9)$$

where: F_s – static force on the weight sensor from weighing container mass; F_d – full dynamic force depending of product mass in the container.



a *b* *c*

Figure 4. *Changes graph: a – acceleration depend on time; b – speed depend on time; c – rod movement depend on time*



a *b*

Figure 5. *Weighing container weight sensor load scheme with production for dosing machine: a – with vibrator; b – with belt feeder*

Dose formation process control in weighing container are reduced to definition of total dynamic force F_d, which are define by the sum of instant weight of the product in the container and dynamic pressure of the product:

$$F_d = m_t \cdot g + F_t \,, \tag{10}$$

where: m_t – current product in weighing container mass value ; g – acceleration of the gravity; F_t – dynamic product pressure on the weighing container.

Current value of the product mass in weighing container:

$$m_t = p \cdot t = B \cdot \delta \cdot \rho \cdot V_0 \cdot t, \,, \tag{11}$$

where: t – dosing operation time, p – product feed intensity; B – product stream from the feeder width.

$m_t \cdot g$ value defines the product mass that we have in the container. So when the feeder will stop the sensor will take load:

$$F_\Sigma = F_d + M_d \cdot g \,, \tag{12}$$

where: M_d – specified dose mass.

Forming and weighing of the dose are made in time, so the main part of total force on weight sensor, which will have influence on dosing accuracy, is the dynamic pressure of the product on the weighing container.

Dynamic pressure value depending on the product flow can be calculated as:

$$F_t = p \cdot V_y = B \cdot \delta \cdot \rho \cdot V_0 \cdot V_y, \tag{13}$$

where: V_y – product flow speed in time when it contacts with the product in container, V_0 – feeder product speed.

F_t value views external force on the weight sensor, but it doesn't view real quantity of the product that will move to the container after the stop of the feeder. To ensure complaints of two loads it is needed to:

$$F_t = m_0 \cdot g, \tag{14}$$

where: m_0 – product mass, which is moving after feeder stop.

For dosing machines scheme on fig.5:

$$m_0 = B \cdot \delta \cdot \rho \cdot y. \tag{15}$$

Then, after expression simplification (13, 14, 15) equation to define the end value of the producte layer, which will move to the weighing container will take the next view:

$$y_k = V_0 \cdot V_y \;/ g. \tag{16}$$

Rational placing of the weighing container relative to working surface of the product movement, can be calculated:

$$y_0 = y_k \; + (2 / 3) \, H \,. \tag{17}$$

The end value of the product layer, which moved to weighing container, relatively to working surface of the product movement with a respect to equation (16) can be calculated as:

- vibrator feeder:

$$y_k = \lambda \cdot V_0^2 \;\cdot \{\lambda + [\,(\,\lambda^2 + \sin^2(\,\alpha\,)\,]^{\,0,5}\} \,/\, g\,; \tag{18}$$

- belt feeder:

$$y_k = (\lambda \cdot V_0)^2 / g + R - \pi \cdot (0,5\pi - \alpha) / (2\pi) \times ...$$
$$...\times (\delta + 2R) + \lambda \cdot V_0 \cdot [V_0^2 \cdot (1 + \lambda^2) - ... \qquad (19)$$
$$... - 2\pi \cdot g \cdot (0,5\pi - \alpha) / (2\pi) \cdot (\delta + 2R) + ...$$
$$... + 4g \cdot R \cdot \sin^2 (0,5\alpha)]^{0,5} / g .$$

where: λ – product flow air resistance coefficient; V_0 – approximated product feeding speed by the working element of the feeder; α – feeder angel relative to the horizon; H – weighing container height; R – driven drum radius of belt feeder; δ – product layer height on the feeder; g – gravity acceleration.

By numerical calculation results of equations (18) and (19) it is defined that the key parameter that defines the rational placing of the weighing container (fig. 6) is the production flow speed when it converge with the carrier plane of the feeder.

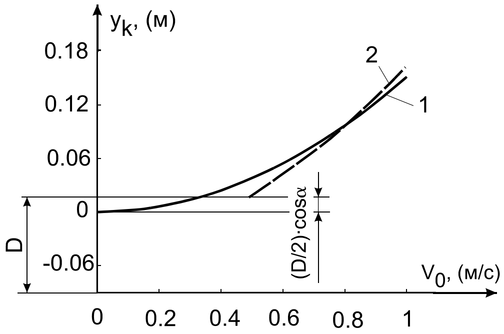


Figure 6. *Weighing container rational* placing *change depending on the product flow speed:*
1 – vibrator;
2 – belt (angel relative to the horizon α = 6°)

Weighing container rational placing deviation relatively to working surface of the product movement decreases dosing accuracy. Modeline part of the dynamic error:

- vibrator feeder:

$$\varepsilon = \gamma \cdot \delta \cdot B \left| y \cdot g - \lambda \cdot V_0 \cdot (V_0^2 \cdot \sin^2\alpha + \ldots \right.$$
$$\left. \ldots + 2 \cdot y \cdot g)^{0.5} \right| / (M_\partial \cdot g) \cdot 100; \qquad (20)$$

- belt feeder:

$$\varepsilon = \gamma \cdot \delta \cdot B \cdot \left| \lambda \cdot V_0 \cdot [V_0^2 + 2 \cdot g \cdot (y - \ldots \right.$$
$$\ldots - R \cdot \cos \alpha)]^{0.5} - g \cdot (y - R + ... \qquad (21)$$
$$... + (0,5 \cdot \pi) / (2 \cdot \pi) \cdot (2 \cdot \pi \cdot R + ...$$
$$\left. ...+ \pi \cdot \delta) \right| / (M_\partial \cdot g) \cdot 100,$$

b – feeder tray width; M_∂ – product dose weight.

III. Conclusions

Created shutter movement mathematics model enables to realize rational working mode of leaner weight dosing machine. Also, as a result of rational placing of weighing container it's possible to minimize the influence of one of the dynamic dosing error parts. One of the technical decisions to regulate the weighing container position relative to feeder working element, can be the installation of weighing system on driven moving guides by which the control is realized.

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QUALITY INDEX OF DAIRY AND VEGETABLE-BASED SEMI-FINISHED PRODUCTS ON BASIS OF PROTEIN CONCENTRATES FROM BUTTERMILK

G. Deynychenko, T. Yudina, I. Nazarenko

Donetsk National M. Tugan - Baranovsky University of Economics and Trade.
Donetsk, Ukraine

Abstract. *The article examines quality index of milk and vegetable-based semi-finished products on basis of protein concentrates from buttermilk. Nutrition and relative biological value, basic safety indexes of developed semi-finished products is defined in the article.*

Key words: dairy and vegetable-based semi-finished product.

Providing the population with biologically valuable nutrition product is the priority of social and economic development of Ukraine.

One of the promising areas of the solution of the problem is the creation of a complex nutrition product composition by combining dairy and vegetable material, which provides the possibility of mutual enrichment of received products with essential ingredients and regulation of their composition in accordance with the basic principles of sensible nutrition [9].

It is known that 60...65% of the daily requirement of protein should be satisfied by products of animal origin due to the fact that they contain more essential amino acids and easier to digest than proteins of plants [2]. However, plant proteins are more common in nature and constitute 68,0...80,0% of the total consumption of all proteins, but most of them are limited by the content of lysine, isoleucine, sulphur-containing amino acids. Substitution of materials of animal origin by vegetable origin reduces calorie value of food, enriches products with vitamins, most of which are powerful antioxidants, dietary fiber, minerals, organic acids, which facilitates the absorption of calcium, phosphorus, iron and other functional ingredients whose presence is necessary for normal functioning of the human body [1]. What is more, note very important physiological phenomenon: when combining heterogeneous origin of protein in the food rations, their digestibility almost always improves [11].

Theoretical and practical basics of nutrition products with adjustable composition and properties contained in the works of local and foreign scientists: O.O. Grinchenka, A.M. Dorohovych, P.A. Karpenko, M.B. Kolesnikov, V.N. Korzun, G.M. Lysyuk, L.P. Babe, L.M. Mostovaya, N.Y. Orlova, M.I. Ordinary, P.P. Pivovarova, N.V. Prytulska et al.

Analysis of international experience as well as trends in the domestic dairy industry proves that it is appropriate to use dairy protein concentrates, including dairy protein concentrate (DPC) with buttermilk for creation of a complex nutrition product composition.

DPC with buttermilk is a product with a homogeneous, soft, with suit texture and it has clean taste and odor characteristic of dairy products, the color from white to white with cream shade.

DPC proteins with buttermilk contain in its composition (except of casein) whey proteins, whose part is 26% from weight of protein. Studies have shown [13] that level of all essential amino acids in DPC proteins with buttermilk exceeds the standard of WHO / FAO [4] indicating the high biological value of the product. DPC with buttermilk is a good source of vital minerals and water-soluble vitamins [13].

Therefore, DPC with buttermilk is a promising material for the production of complex composition products, which was taken into account when conducting further research.

The scientific school of Professor G.V. Deynychenka in Ukraine developed several technologies of semi-finished products and nutrition products based on or using concentrate from buttermilk during recent years. [3;7]. But today their range is not wide enough, and there is no technology of dairy and vegetable-based semi-finished products. Therefore, scientific reasoning and development of competitive technologies technology of dairy and vegetable-based semi-finished products is an urgent task, the solution of which will expand the range of products with improved nutritional and biological value and to obtain products with desired functional properties.

Based on the data obtained during the experiments, taking into account the information contained in the scientific and technical literature, we have developed technology to produce dairy and vegetable-based semi-finished products. Developed technologies include the use of concentrate from buttermilk as a main component, and also the introduction of the semi-vegetable puree of carrots, pumpkins and zucchini, egg, wheat flour, sugar.

Technology features, specificity of prescription components and perspectives of further use of technologies developed by dairy and vegetable-based semi-finished products in food identified the need to study their quality indexes.

The aim of this work is to study the quality indexes of dairy and vegetable-based semi-finished products on basis of protein concentrate from buttermilk.

Nutrition products quality is a set of properties that characterize the nutritional and biological value, functionality and technology, health and safety indexes of the product as well as degree of their intensity [12].

Characteristics semi-finished minced sour crude are chosen for control in establishing of quality indexes of the developed semi-finished products. The content of the nutrients in dairy and vegetable-based semi-finished products and the reference sample are shown in Table 1.

Analysis of the data Table 1 indicates that the developed products exceed the reference sample according to the contents of most nutrients. Thus, according to the content of solids milky and carrot semi-finished product exceeds the control by 5,27%, semi-finished milk pumpkin - by 6,32%, semi-finished milk zucchini - by 2,05%.

It is found (Table 1), that the defined semi-finished products exceed control in fat by 0,80...0,82%. This is due to the use of DPC with buttermilk formula, the content of fat in which is 1,34%, against 0,60% in fatless sour crude.

Table 1. *The chemical composition of dairy and vegetable-based semi-finished products, % ($\overline{X}$ ±m)*

Index	Con-trol	Semi-finished products		
		milky and carrot	milky and pumpkin	zucchini and milky
solids	30,5	35,77±1,1	36,82±1,1	31,55±1,1
white	17,2	14,06±0,5	13,99±0,5	15,79±0,6
fat	1,00	1,82±0,07	1,81±0,08	1,80±0,07
Carbohydra-tes,including				
mono - and disacchari-des	10,0	14,28±0,5	13,94±0,6	3,99±0,12
starch	1,10	2,41±0,10	2,75±0,10	5,42±0,14
cellulose	-	0,17±0,01	0,17±0,01	0,05±0,01
pectin	-	0,37±0,01	1,63±0,05	0,58±0,03
ash	1,10	1,62±0,07	1,52±0,06	1,65±0,06
Caloric, kkal/100h	109,0	129±4,9	133±5,0	97,73±3,7

Due to the replacement of part of materials of animal origin to vegetable one and added sugar, developed semi-finished products (milky and carrot, milky and pumpkin) exceed control at the content of mono-and disaccharides by 4,28%, and 3,94% respectively.

It is known [5] that soluble fibre, especially pectin, has a positive effect on digestion and cholesterol metabolism in humans. It should be noted that the pectin content was 0,37%, 1,63% and 0,58% respectively in developed semi-finished products (milky and carrot, milky and pumpkin, zucchini and milky).

Data in the Table. 1 show that the replacement materials, which contain protein to materials for vegetable, puree resulted in a decrease of 8,20...18,66% of proteins in developed products. However, analysis of the quality of the proteins (Table 2) shows that there was identified and quantified 18 amino acids including all essential in he developed semi-finished products.

As it is seen form from the Table 2, proteins of dairy and vegetable-based semi-finished products have particularly high content of leucine (8,48...8,54% of the total amino acid and 22,39...22,67% of the essential amino acids), lysine (respectively 6,79...6,83% and 17,84...18,03%), valine (respectively 6,55…6.58% and 17,36...17,40%).

Table 2. *Amino acid composition of proteins in semi-finished dairy and vegetable products, ($\overline{X}$ ±m, $m \le 0,05$)*

Name amino acids	Control	Semi-finished products		
		milky and carrot	milky and pumpkin	zucchini and milky
Essential:	7,067	5,190	5,179	5,845
valine	1,021	0,901	0,900	1,017
isoleucine	0,838	0,663	0,662	0,751
leucine	1,555	1,162	1,163	1,325
lysine	1,208	0,930	0,934	1,043
methionine	0,472	0,337	0,337	0,374
threonine	0,789	0,598	0,598	0,671
tryptophan	0,258	0,153	0,153	0,171
phenylalanine	0,926	0,433	0,433	0,493
Nonessential:	9,988	8,505	8,491	9,679

alanine	0,618	0,388	0,384	0,433
arginine	0,728	0,444	0,446	0,498
aspartic acid	1,155	1,322	1,316	1,472
histidine	0,534	0,334	0,334	0,378
glycine	0,343	0,201	0,200	0,230
glutamic acid	2,978	2,841	2,830	3,269
proline	1,522	0,664	0,663	0,780
serine	0,984	1,489	1,491	1,686
tyrosine	1,018	0,583	0,588	0,660
cystine	0,108	0,240	0,239	0,273
Total	17,055	13,695	13,670	15,524

As for nonessential amino-acids in dairy and vegetable-based semi-finished products, there is a high maintenance aspartic (9,48...9,65% of the total amino acids), glutamine (20,70...21,05%) acids and serine (10,86...10,91%), which is typical for dairy products.

To determine the biological value of proteins the most widely used in practice are methods of amino acid scales based on the use of amino acid swift [4], an integrated indicator amino acid Kyunau-Auxerre-Mitchell [8;10] and index Korpach [6]. The last two did not become popular because of the great complexity of the calculations and now the most commonly used method for determining the amino in the modification proposed by the FAO / WHO, which allows to identify the so-called limiting amino acids.

Calculation of essential amino acids in products and its comparison with the standard data of the FAO / WHO showed that there is no proteins within limiting amino acids in dairy and vegetable-based semi-finished products, levels of all essential amino acids exceeds standard of FAO / WHO, which indicates a high biological value of products.

On the one side, the biological value of the product is defined by matched speedy settlement of essential amino acids to standard of FAO / WHO, but on the other side, it is defined by the degree of hydrolizability of proteins by enzymes digestive track.

Information about the extent of digestibility and relative biological value (RBV) of developed semi-finished products is presented in Table 3.

Table 3. *The degree of digestion and relative biological value of dairy and vegetable semi-finished products, ($\overline{X}$ ±m)*

Name of products	The extent of digestibility, g / eq %			RBV
	pepsin	trypsin	total	
Kazeïn control	5,05±0,14	25,38±0,79	30,43±0,94	100
Semi-finished products				
milky and carrot	6,00±0,19	23,2±0,63	29,20±0,85	142±3,8
milky and pumpkin	5,93±0,17	22,7±0,73	28,63±0,89	143±4,5
zucchini and milky	5,89±0,21	22,4±0,60	28,29±0,76	141±3,4

According to the data in Table. 3, proteins developed by dairy and vegetable semi-finished products are characterized by a high degree of digestion and superior control (casein) in terms RBV of 1,41...1,43.

Adding vegetable material to composition of semi-finished products helps to enrich products with minerals.

The results of the research have showed that according to the contents of all ashy mineral elements, developed semi-finished products exceed control. However, for assessing the nutritional value the proportion of these elements is more important than the absolute content of these elements in the developed products. According to the formula of a balanced diet from FAO / WHO, the best ratio is Ca: P: Mg - 1:1,5:0,5. This ratio equals to semi-finished dairy and carrot product -1:1,52:0,33 dairy and pumpkin product - 1:1,53:0,31, dairy and zucchini product - 1:1,47:0,28 . It does not exactly correspond to the formula of balanced diet, as the content magnesium is a bit lowered. However, this level of magnesium content is typical for milk and dairy products. For example, in the reference sample, this ratio is 1:1,64:0,21.

The results of study of vitamin content of the examined products have shown that the developed semi-finished products significantly exceed the control level at the content of B vitamins, β-carotene, vitamin E, C, E, A. For example, the content of vitamin B_1 in developed semi-finished products compared with a control sample was increased by 9,8...11,2 times, vitamin B_2 - by 7,58…8,54 times, and vitamin B_6 - by 26,8 to 24,2 ... again. In developed semi-finished products: dairy and carrot, dairy and pumpkin, and dairy and zucchini the contents of β-carotene is 2,71, 9,63 and 0,13 mg/100g, vitamin C – 2,80, 3,27 and 3,51 mg / 100 g% respectively.

The main safety indicators of dairy and vegetable-based semi-finished products and reasonable parameters for their storage have been defined. It was found that the optimal parameters for storing semi-finished products under which all technological properties are kept high are when the temperature is 0 ... 2°C, relative humidity is 80...85%, storage time - 10 days. It was determined developed semi-finished products do not exceed the maximum allowable concentrations and meet regulatory documents according to the toxicological and radiological indicators.

The article examines quality index of milk and vegetable-based semi-finished products on basis of protein concentrates from buttermilk. Nutrition and relative biological value, basic safety indexes of developed semi-finished products is defined in the article.

The results of the search have showed that developed semi-finished products exceed the control as for the content of major dietary nutrients.

It was found that there is no limiting amino acids in content of proteins of semi-finished products the level of all essential amino acids exceeds the standard of FAO / WHO.

The basic parameters of safety of dairy and vegetable-based semi-finished products are studied and reasonable parameters for storage are indicated.

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THE DYNAMICS OF THE CHEMICAL INDICES OF A BUTTER PROCESSED BY A HIGH CYCLICAL PRESSURE IN TIME AS QUALITY STABILITY PARAMETER

V. Sukmanov, S. Gromov

Institute of Food Industry of Donetsk National University of Economics and Trade named Mikhail Tugan-Baranovsky

Abstract. *As a result of experimental studies the character of influence of a butter processing by a high cyclic pressure on the change of dynamics of its chemical indices (peroxide, iodine, acidity, saponification indices, Polenske, Reihert-Meissl indices)which characterize its durability and quality stability during long-time storage have been determined.*

Key words: butter, durability during long-time storage, high cyclic pressure, peroxide index, iodine index, acidity index, saponification index, Polenske, Reihert-Meissl indices.

As all fats butter is not durable in the process of long-time storage. Instability of fats in storage is revealed in rancidification, i.e. deterioration in taste and flavor and consequently deterioration of the quality of butter which even follows to the non-applicability for use as a food. Unfortunately, butter produced now has some inherent drawbacks decreasing its consumer values, nutritional and energy values. Such defects can be found even in a fresh butter, but those defects are developed intensively in the process of product storage.

Such defects are caused by the action of anaerobic external micro-flora, fungi as well as oxidization processes of fats spoilage. Putrefactive anaerobic bacteria, yeast, fungi, fluorescing bacteria take part in the development of such defects. Under the influence of the enzymes emitted by these micro-organisms the decomposition of fats, peptonization of proteins and oxidization of fats under the influence of air oxygen occur in the surface layer of butter.

Deterioration of taste and flavor of edible fats is only the external exposure of some complex chemical transformations of fats in the course of oxidation therefore they substantially lose the edible value, and frequently become also unsuitable for edible use.

Oxidative rancidification is the most widespread type of damage of fats in the course of their storage and is the result of complex chemical and biochemical reactions.

One of the most widespread consequences of spontaneous oxidation of fats is the loss of its vitamine properties both owing to oxidation decomposition of highly unsaturated fatty acids and as a result of destruction of vitamins by the oxidants to have been contained in fats.

For the purpose of decrease of the oxidative processes rates during storage of butter and increase of its consumer properties the technology of high cyclic pressure (HCP) has been applied.

Processing of butter by HCP method leads to changes of its properties which are described by corresponding chemical indices (peroxide, iodine, acid, saponification ratio, Polenske and Rejhert-Meissl indices) which characterize the firmness of a product in the course of storage.

The purpose of the present work is estimation of influence of processing of butter by HCP on dynamics of change of its chemical indices characterizing its firmness and quality stability in the course of long-term storage.

The object of research. The low fat farmer’s butter (72, 5 %) produced from a sweet cream by Maruanka milk plant, JSC "LAKTIS". The butter is manufactured according to DSTU standard 4399:2005 (The State Standard of the Ukraine) «Butter. Technical specifications».

Considering the results of the former studies on the influence of HCP parameters on microbiologic sterility and rheological characteristics of butter, the area of variation of parameters values of HCP processing has been defined:

- Maximum pressure P_{max} = 230 and 350 MPa, number of loading cycles n – 2 and 5; impulse speed at the pressure increase $\upsilon_{и\uparrow}$ = 1 MPA/sec and 10 MPA/sec, impulse speed at the pressure decrease $\upsilon_{и\downarrow}$ = 5 MPA/sec and 25 MPA/ sec;

Duration of the cyclogram fields in the extreme upper and lower points – 30 sec. The oil temperature - $15\pm0,5^0$C that corresponds to temperature at the moment of its escaping from the butter former. A profile of the process cyclogram it shown on the Figure 1.

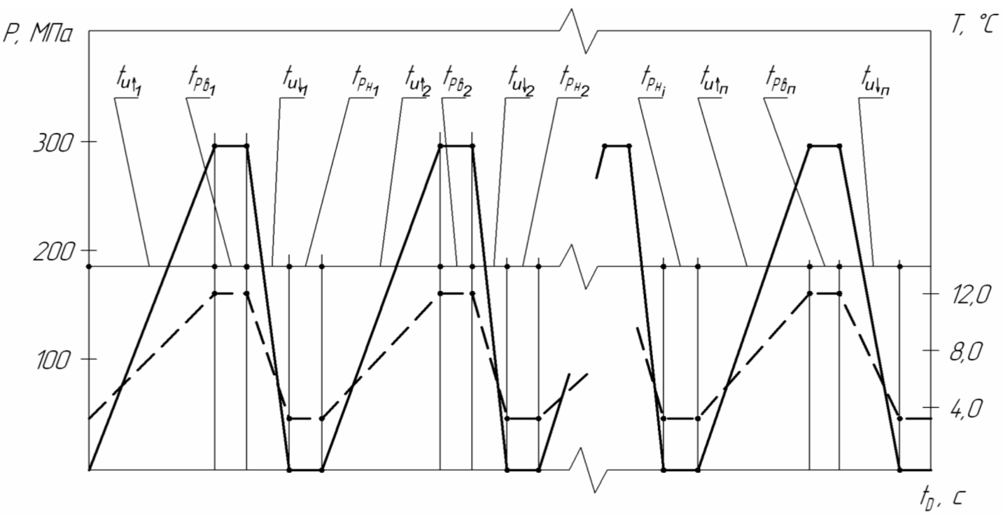

Fig. 1. *The process cyclogram of processing of butter by HCP*

$t_{u\uparrow 1}$, $t_{u\downarrow 1}$ – first pulse duration at the pressure increase; $t_{P\text{в}1}$, $t_{P\text{н}1}$ – duration of the pressure hold in the first upper and lower points of the cyclogram; $t_{P\text{н}i}$ - duration of the pressure hold in the *i* -fold (*i*=1 … *n*) upper point of the cyclogram; $t_{u\uparrow i}$, $t_{u\downarrow i}$ - duration *n* – fold pulse at the pressure increase and decrease

Duration of the pressure holds in the first upper and lower points of the cyclogram $t_{P\text{в}}$, $t_{P\text{н}}$ equal 30 seconds has been selected. The temperature of butter during HCP processing - 15±0,5^{0}C that corresponds to the temperature of butter at the moment of its release from the butter former. Number of cycles – from 1 to 5.

All investigated samples have been stored within 12 months. Storage temperature - (4±0,5^{0}C). The butter samples have been sampled in the summer season (June 2011 and repeated control measurements have been performed in June 2012). Thus annual deviations for the parameters under control comprise not more than 5 %.

In production of butter with the use of HCP the technological parameters of this process (number of loading cycles – ***n***; the maximum pressure value in each cycle - $\mathbf{P_{max}}$, MPa; the rate of pressure rise and pressure relief - $\boldsymbol{\upsilon_{\text{и}\uparrow}}$, $\boldsymbol{\upsilon_{\text{и}\downarrow}}$, MPa/sec; process temperature – **t**, ^{0}C) in many respects define the butter structure and quality of a product received.

The research complex for butter processing by HCP. For the study of influence of butter processing parameters by HCP on chemical indices the research complex created in the problem research laboratory named «The use of high pressure in production of edible productions» of the Donetsk national university of economy and trade named after Mikhail Tugan-Baranovsky has been used.

The processing of the samples by high pressure (HP) under study has been performed in sealed soft containers which have been placed into the working chamber of the high pressure apparatus.

The reference sample of butter and the samples subjected to processing by HCP and the subsequent analysis on investigated indexes have been studied in compliance with the technical conditions adopted by the Marianka milk plant, JSC "LAKTIS".

Physical and chemical indices of a reference specimen after the release of butter sample from the butter former: *PN* – 0,024 (½O_2)/kg; *IN* – 30 г I_2/100 g; *KN* – 1,15 mgKOH/g; *Pol. n* – 3,15; *R-M n* – 26,5; *SN* – 228 mgKOH/g.

The influence of process parameters of butter processing by HCP on the dynamics of its chemical indices in time. The structure of butter continues to be formed within several days after the release of butter from the butter former. The oxidation processes in butter proceed in the presence of oxygen which is present at a product in the form of air bulbs to which the surface layers of the product is contacting. The gas phase volume in a freshly produced butter comprises 1—13 ml per 100 grams. The gaseous phase is represented by air bubbles and a dissolved air. In the course of storage the oxygen content quickly decreases.

As a result of processing of butter by HCP dispersity of the butter structure (fat balls – moisture particles – air bubbles) has been changed and the volume of air bubbles is decreased since the part of air bubbles is destroyed, passed into the plasma and further does not take part in process of fat oxidation.

The sealed packaging of reference specimens of butter and the samples treated by HCP (absence of contact of a product with the external oxygen) leads to the fact that the content of the oxygen which is present in air bubbles on the initial stage of storage of butter as a result of oxidizing reactions aspires to zero and further oxidative processes are being retended and are practically stopped that has been proved by the results of experimental studies.

The circumstances set forth above have allowed putting forward with the assumption that the processing of butter by HCP leads to change of chemical indexes of butter as directly after its release, as well as in the process of its long-term storage.

The methods of defining of chemical indexes of butter. Iodine index (*IN*) specifies the general unsaturation and quality of fats. *IN* shows quantity of grams of iodine which can be bonded to 100 g of fat. The value of this index testifies the prevalence of the saturated or unsaturated fatty acids in fats. The higher is the content of unsaturated fatty acids in fat, the higher is *IN* value. *IN* value characterizes a degree of freshness of fats. During oxidation of fats in the course of storage *IN* value decreases.

IN of fat is one of the major indexes of oils and fats which characterizes a degree of unsaturation of fat, its ability to oxidation, drying, hydrogen bonding. *IN* has been defined by the method of Kaufmann in accordance with the GOST R ISO 3961-2010 (the State standards of the Russian Federation) «Fats and oils of animal and vegetable origin. Iodine test».

Acid index *(KN)* defines the content of free fatty acids contained in 1 g of fat. It is expressed by quantity of mg of the pyretic potassium, necessary for their neutralization and is the major index of quality of edible fats.

KN index of butter has been defined according to GOST R 50457-92 (ISO 660-83) «Fats and oils of animal and vegetable origin. Acid index and acidity definition».

The Reihert-Meissl index (***R-M n***) is defined as the quantity of the water soluble volatile fatty acids contained in oil or fat. The Polenske index (***Pol. n***) characterizes the content of water-insoluble volatile fatty acids, mainly caprylic, pelargonic, capric ones contained in 5 g of fat; it is expressed in mg of pyretic potassium. Values of (***R-M n***) and ***Pol n*** are increase at oxidation of fats.

Pol n characterizes the presence of low molecular weight volatile water-insoluble fatty acids (caprylic, capric and partially lauric ones) in 5 g of fat. The essence of the method consists in defining of the volume of 0,1 mole/l solution of sodium oxyhydroxide spent on neutralization of volatile water-insoluble fatty acids (caprylic, capric, caproic ones), contained in 5 g of fat after its saponification.

The indexes ***R-M n*** and ***Pol N*** have been defined according to GOST 10766-64 «Coconut Oil. Technical conditions».

Saponification ratio (*SN*) is the ratio of mass of the potassium hydroxide spent on saponification of glycerides (bonded fatty acids) and neutralization of the free fatty acids contained in oil, to the mass of the sampling. It characterizes the mean molecular weight of a mixture of fatty acids of fat: the lower molecular weight acids are contained in it, the higher is the value. *SN* index has been defined according to GOST 5478-90 «Oils of vegetable and natural origin; fatty acids. A method of defining of saponification ratio».

The method of defining of the peroxide value (*PN*) according to GOST P 51487-99. «Oils of vegetable origin and fats of animal origin. The method of defining of peroxide value» is based on reaction of interaction of oxidants of vegetable oils and animal fats (peroxides and hydro peroxides) with potassium iodide in acetic acid and isooctane solution or chloroform with the subsequent quantitative definition of the emitted iodine by sodium thiosulfate solution by a titrometric method. For the purpose of this research the method with chloroform application has been used.

Processing and the analysis of experimental data have allowed to receive the information characterising the influence of parametres of processing of butter by HCP on the dynamics of its chemical indexes in the course of long-term storage. As an example, the Fig. 2 represents the dependences of change of chemical indexes of the butter treated by HCP at P_{max}=350 MPa; where: n = 5; $\upsilon_{\text{и}\uparrow}$ =10 MPa/sec; $\upsilon_{\text{и}\downarrow}$ = 25 MPa/sec.

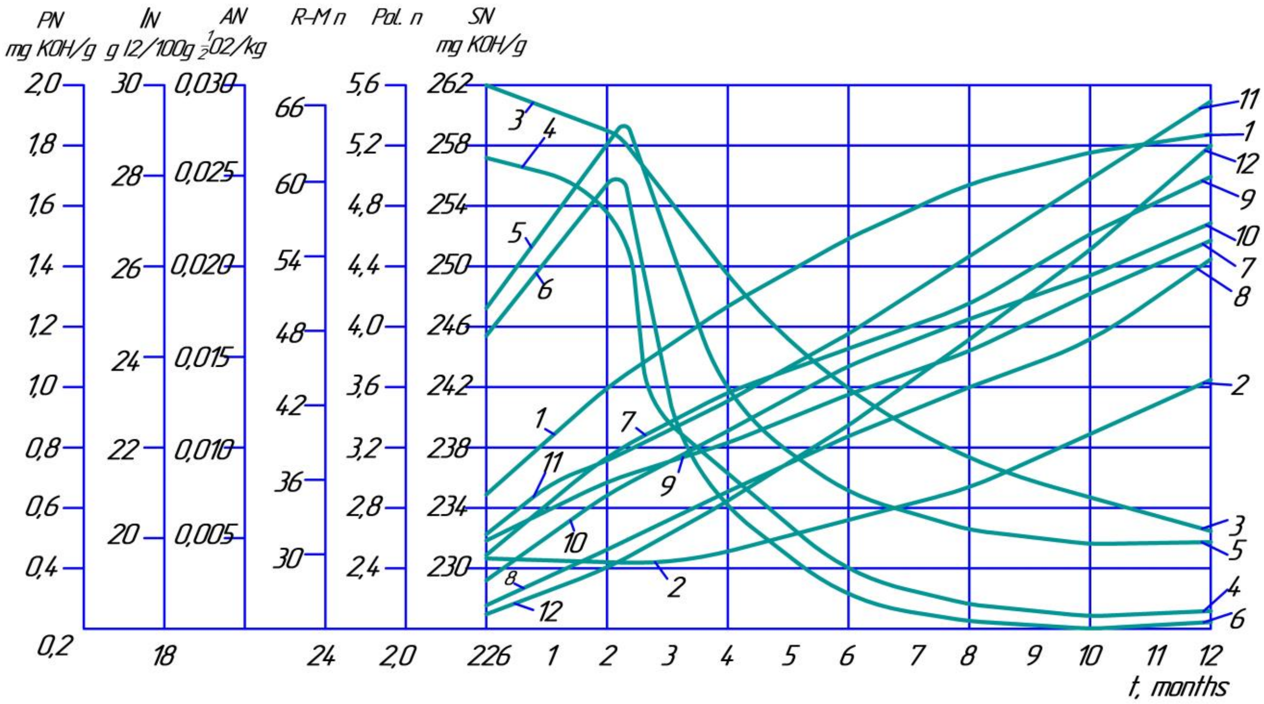

Fig. 2. *Change of chemical numbers of samples of the butter treated by high cyclic pressure at P_{max}=350 MPa; n = 5; $\upsilon_{u\uparrow}$ =10 MPA/sec; $\upsilon_{u\downarrow}$ = 25 MPA/sec (notations without indexes) and reference specimens (a notation with an index "to") in the course of storage.*

1-KN_K; 2-KN; 3-IN_K; 4-IN; 5-PN_K; 6-PN; 7-Pol. n_K; 8-Pol. n; 9- R-M n_K; 10-R-M n; 11-SN_K; 12-SN

Based on the results of experimental studies it has been proved that in the course of storage of butter sample, in the first 2 months the acid index (*KN*) (Fig. 1) - one of the major qualitative parameters of butter characterizing the rate and depth of butter hydrolysis, i.e. the quantity of free fatty acids in fat, in the butter reference specimens grow more intensively (in 1,6 times), than at the samples treated by HCP: depending on the process parameters providing different quantity of oxygen in butter where the acid index increases by 1,16 – 1,03 times.

The content of oxygen which provides oxidation of fat in the course of its further storage in reference specimens appeared to be higher; thus in samples of the butter treated by HCP the growth of acid index less intensive at any process parameters; after 12 months of storage of butter the acid index *KN* in the reference specimens was equal to 1, 86 mgKOH/gr and in samples of the butter treated by HCP – 1, 49 – 1, 02 mgKOH/gr depending on process parameters.

For the purpose of mathematical description and the analysis of the dependences given on the Fig 2, the application program named STATISTICA V5.5A that has allowed receiving the functions describing the change of values of chemical indexes in the course of storage at various process parameters of butter processing by HCP has been used:

$$KN_i = a_i + b_i \cdot \tau + c_i \cdot \tau^2, \qquad (1)$$

where KN_i is the value of *KN* index for butter, gained with the use of HCP at process parameters i = *f* (P_{max}, *n*, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$);

- a_i, c_i, b_i – quotients of the equations with the corresponding process parameters *i* = *f* (P_{max}, *n*, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$).

Generally *PN* index in the butter increases at the expense of oxidation of triglycerides by air oxygen. However the objects of research are the samples of butter hermetically sealed. Thus, the processing of butter by HCP has led to reduction of moisture content in investigated samples and to essential reduction of the air bubbles. Hence, the area of contact of a moisture with triglycerides decreases, and less hydrolysates are formed. The situation with process of oxidation of triglycerides is similar. Thus, the processing of butter by HCP promotes to reduction of hydrolysates and oxidation in butter.

Within the first 2 months of storage the oxygen which is present both in reference specimens and in the samples treated by HCP leads to the increasing of *PN* values in a reference specimen in 1,5 times, and in the samples under testing – in 1,35 - 1, 37 times. Furthermore, in a reference specimen an insignificant decrease of *PN* value begins due to reaction with the remained quantity of oxygen; in samples of the butter treated by HCP the quantity of oxygen is essentially less that leads to essential decrease in *PN* value: by 1,71 - 1, 73 times for the butter samples under testing. Further on, the decrease rate of *PN* value for samples treated and for the control samples are almost equal and in 5 months of storage this PN value for the reference specimen is equal 0,0118 (1/2 O_2) / kg and in pre-treated samples 0,013 - 0,014 (1/2 O_2) / kg accordingly. In the course of the further storage some fluctuation of PN values is observed with a tendency for reduction that can be explained by practical absence of oxygen necessary for oxidation of triglycerides.

For the mathematical description of *PN* value change in the course of storage the function (2) has been used. The confidence interval – 0,95.

$$PN_i = a_i + \frac{e^{-b_i \cdot \tau}}{c_i + d_i\tau + g_i\tau^2}\ , \qquad (2)$$

where PN_i – the value of *PN* index in butter produced with the use of HCP with the process parameters i = f (P_{max}, n, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$);

- a_i, c_i, b_i d_i, g_i - quotients of the equations with the corresponding process parameters $i = f$ (P_{max}, n, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$).

Immediately after the processing of butter by HCP its *IN* value has been reduced from 30 to 28,4. Further on, in the course of storage the decrease of ЙЧ value in all samples has occurred, however for the first three months of storage in pre-treated samples this index has dropped by 1,33 - 1,25 times while in the control sample the this index has dropped only by 1,14 times. Further on, rates of decrease in this index in samples under testing continues to drop and in 12 months of storage it equals to 20,5 g I_2/100 in the reference specimen *IN*; in pre-treated samples – 19,5 - 19,1 g I_2/100 Thus, the processing of butter by HCP essentially influences on the quantity of unsaturated fatty acid in the course of storage of butter. One of the possible causes of such effect is lower oxidability of butter after processing by HCP and hence, presence of smaller number of radicals capable as a result of recombination to form the multiple bonds which quantity defines iodine index value in the sample.

Taking into account the character of experimental curves they have been described by the use of segmental and linear regression [162 (3) and values of the point (*c*) of the second order curves break of are received.

$$IN_i = \begin{cases} a_i + b_i e^{-\frac{\tau - c}{d_i}} & \tau < c \\ a_i + b_i e^{-\frac{\tau - c}{g_i}} & \tau > c \end{cases}, \qquad (3)$$

where SN_i - *SN* index value for butter, produced with use of HCP with the process parameters i = f (P_{max}, n, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$);

- a_i, c_i, b_i, d_i, g_i – quotients of the equations with the corresponding process parameters $i = f$ (P_{max}, n, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$).

The higher is the content of low molecular weight acids in a milk fat, the higher is the SN value. The given index in pre-treaded samples within 2 months of storage has grown slightly: from 226 to 228 - 230 accordingly; in the reference specimen the given index equals to 240. Further on, in the reference specimen within the next two month the decrease of the given index value up to 238 occurred; the given index has continued to grow in pre-treated samples up to values 234 – 235. The decrease of the index value gained at all samples has occurred and in 12 months in the reference specimen the SN value equals to 263, while in the pre-treaded samples this value equals to 256 – 258.

The graphic dependences shown on Fig. 2 have been presented by the function (4) describing the change of *SN* values in the course of storage at various process parameters of butter processing by HCP. The confidence interval – 0,95.

$$SN_i = a_i + b_i\tau^2 + c_i\sqrt{\tau}\ , \qquad (4)$$

where SN_i is the value of SN index for butter gained with the use of HCP at the process parameters i = f (P_{max}, n, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$);

- a_i, c_i, b_i – quotients of the equations with the corresponding process parameters $i = f$ (P_{max}, n, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$).

The content of water soluble volatile fatty acids contained butter – *R-M n*, and the content of water insoluble volatile fatty acids contained butter or fat – *Pol. n.* also increases in the butter reference specimens in the first 2 months after its production more intensively. *Pol. n.* value in first two months of storage in a reference specimen has increased by 1,4 times and in pre-treated test samples – in 1,3 times; further on by the third month of storage in a reference specimen the said index has been reduced in 1,05 times while in pre-treated test samples the said parameter has been reduced but 1,17 - 1,16 times. In the course of the further storage the *Pol. n* value in all samples continuously increased and in 12 months of storage for the reference specimen it has been equal to 5,3 and for pre-treated test samples – 4, 6 and 4,8 accordingly.

The graphic dependences shown on the Fig. 2, have been presented by the function (5), describing the change of values *Pol. n.* in the course of storage at various process parameters of butter processing by HCP. The Confidence interval – 0,95.

$$Pol.n = a_i + b_i \tau^2 + c_i \sqrt{\tau} \qquad (5)$$

where *Pol. n.* is the value of *Pol. n.* index for butter gained with the use of HCP at process parameters $i = f\,(P_{max}, n, \upsilon_{и\uparrow}, \upsilon_{и\downarrow})$;

- a_i, c_i, b_i are quotients of the equations with the corresponding process parameters $i = f\,(P_{max}, n, \upsilon_{и\uparrow}, \upsilon_{и\downarrow})$.

The similar pattern occurred during the investigation of dynamics of *R-M n.* Index. In first two months of storage the said index has been increasing at the most intensive rate in the reference specimen: from 26,5 to 40,5 (in 1,53 times); the decrease of the given index in pre-treated test samples comprises 1,48 - 1,46 times. Further on, by the third month of storage the decrease of *R-M n.* Index value up to 38,5 in the reference specimen and up to 33,0 - 34,5 in pre-treated test samples has occurred; then there has been the period of almost monotonous increase of the gained index both in the reference sample and in the pre-treated test samples. In 12 months of storage in a reference specimen the value of *R-M n.* Index equals to 62,0 and in pre-treated test samples – 57,5 - 59,0.

The graphic dependences shown on the fig. 3, have been presented by the function (6), describing the change of *R-M n.* index values in the course of storage at various process parameters of butter processing by HCP. The Confidence interval – 0,95.

$$R - Mn = a_i + b_i \tau^2 + c_i \sqrt{\tau} \qquad (6)$$

where $R\text{-}M\ n_i$ is the value of *R-M n* index in butter produced with the use of HCP with the process parameters $i = f\,(P_{max}, n, \upsilon_{и\uparrow}, \upsilon_{и\downarrow})$;

- a_i, c_i, b_i – quotients of the equations at the corresponding process parameters

$i = f\,(P_{max}, n, \upsilon_{и\uparrow}, \upsilon_{и\downarrow})$.

Conclusions.

Thus, in the course of experimental studies the functional dependences of chemical indexes of butter characterizing its firmness and quality stability in the process of long-term storage on the process parameters of butter processing by HCP has been defined. It has been shown that the increase of the process parameters values in processing of butter by HCP ($\boldsymbol{P_{max}}$, $\boldsymbol{n}$, $\upsilon_{и\uparrow}$, $\upsilon_{и\downarrow}$) leads to the increase of its stability in the course of storage and to enriching of its properties which are characterized by the corresponding chemical indexes.

The rate of KN index increase in samples of the butter treated by HCP it is essential lower compared to the gained index in a reference specimen. For the first 2 months of storage of butter *KN* index for the samples treated by HCP has been increased in 1, 16 – 1,03 times depending on process parameters while the given index for the reference sample has been increased by 1,6 times which can be explained by the fact that the content of oxygen providing oxidation of fat in the course of its storage in the reference specimens is higher than in the pre-treaded samples. In the samples of the butter treated by HCP the growth rate of *KN* index is sufficiently lower with any process parameters and after 12 months of storage of butter the value of *KN* index in the reference specimens has been equal to 1,86 mg KOH/gr and in samples of the butter treated by HCP this index equals to 1,49 – 1,02 mg KOH/gr depending on the parameters of processing.

Processing of butter by HCP promotes to the reduction of hydrolysates and oxidation. In the first 2 months of storage the oxygen which is present both in reference and in the samples treated by HCP leads to the increase of *PN* values in the reference specimen in 1,5 times, and in pre-treated test samples in 1,35 - 1, 37 times. Further on, in the reference specimen the insignificant decrease of *PN* value begins due to the reaction with the remained quantity of oxygen; in samples of the butter treated by HCP the content of oxygen is sufficiently lower which leads to the essential decrease of *PN* value: in 1,71 - 1, 73 times. Further on, the decrease rates of *PN* value in the pre-treated and the reference samples are almost equal and in 5 months of storage in the reference specimen the *PN* value is equal to 0,0118 (1/2 O_2) / kg and in pre-treated test samples 0,013 - 0,014 (1/2 O_2) / kg. In the course of the further storage some fluctuation of *PN* values with the tendency to reduction of values has been observed which fact can be explained by a practical absence of the oxygen necessary for oxidation of triglycerides.

Immediately after the processing of butter by HCP, the value *IN* value drops from 30 to 28,4. Further on, in the course of storage the decrease of *IN* value in all samples has occurred, however for the first three months of storage in pre-treated test samples the gained index has dropped by 1,33 - 1,25 times while in the reference sample the gained index has dropped only by 1,14 times. Further on, the decrease rates of the given index in the samples under testing drop and in 12 months of storage the *IN* value for the reference specimen has been equal to 20,5 g I_2/100 while in pre-treated test samples this value equals to 19,5 - 19,1 g I_2/100. Considering the character of experimental curves, they have been described with the use of segmental and linear regression.

Within the first 2 months of storage the *SN* index in the pre-treated test samples has grown slightly: from 226 to 228 and 230 accordingly; in the reference specimen the given index has been equal to 240. Further on, the decrease of the given index in all samples has occurred, and in 12 months the *SN* value in the reference specimen *SN been* equal to 263 while in the pre-treated test samples 256 - 258.

The content of water soluble volatile fatty acids (Reihert-Meissl index - *R-M n*), and the content of water insoluble volatile fatty acids (Polenske index – *Pol. n)*, contained in butter have been increasing in the reference sample and in the pre-treated butter test samples in the first 2 months after its production. So, the *Pol. n* value in first two months of storage in a reference specimen has been increased by 1,4 times while in pre-treated test samples by1,3 times and then by the third month of storage in the reference specimen the given index has dropped by 1,05 times while in pre-treated test samples the given parameter has dropped by1,17 - 1,16 times. In the course of further storage the *Pol. n* index value in all samples have been continuously increasing and in 12 months of storage for the reference specimen it equals to 5,3 and for the pre-treated test samples to 4, 6 - 4,8.

In the first two months of storage the value of *R-M n* has been intensively increasing in the reference specimen: from 26,5 to 40,5 (by 1,53 times); the increase of the given index in the pre-treated test samples has been equal to 1,48 - 1,46 times. Further on, by the third month of storage the decrease of *Pol. n* value to 38,5 in a reference specimen and to 33,0 - 34,5 in pre-treated test samples has occurred; then the period of almost monotonous increase of the given index has been observed both in the reference and in the pre-treated test samples. In 12 months of storage in the reference specimen the R-*M n* index has been equal to 62,0 and in the reference specimens to 57,5 - 59,0.

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FORMATION OF AROMATIC PROFILE OF ROSE TABLE WINES MADE OF PINOT NOIR AND CABERNET-SAUVIGNON

M. Bilko, A. Tenetka

National University of Food Technologies, Kyiv, Ukraine

tenetka@gmail.com

Abstract: *This research article presents the study of the aromatic complex of pink table wines. The objects of research were rose dry wines made of Pinot Noir and Cabernet-Sauvignon. Wines were prepared in conditions of micro winemaking by the schemes that included processing without maceration, maceration on mash 3 and 6 hours, mash fermentation to alcohol content by 2% vol. All samples were organoleptically evaluated, which revealed that rose wines from Pinot Noir have more bright and varied aromas. Then varietal characteristics started to appear in wines of Cabernet Sauvignon.*

Also in the obtained samples the qualitative composition and quantitative content of aroma complex by gas-liquid chromatography was determined. The percentage of the main groups of substances responsible for the aroma of pink table wines was determined. Main representatives of the higher alcohols, esters, acids, and lactones, which cause particular flavor of this type of wine, were found.

Key words: rose wine, aroma compounds, berry tones, Pinot Noir, Cabernet Sauvignon, lactones, higher alcohols, esters, fatty acids, gas-liquid chromatography.

I. Introduction

Aroma is one of the main wine quality indicators. Along with the color it can play a paramount role. Its feature is the presence of fruit and berry tones in aroma of rose wines - barberry, dogwood, raspberry, strawberry, red currant. Dairy tones (including cream) are also quite common [2,6,9]. In contrast to wines with varietal aroma characters, determining factors in the formation of rose wines aromatic profile are technological methods of processing grapes and fermentation conditions, e.g. yeast strain [1, 8, 10]. The main stage in the flavor formation of this type of wine occurs during fermentation, when the majority of fruity flavored esters and feraneols are formed. [4, 8, 9].

Various aromatic compounds can contribute differently in formation of aromatic profiles of rosés depending on their concentrations in the wines and the presence of other components that may enhance aromatic aspects of each other on the principle of synergy [5, 7].

For example, terpenoids, fatty acid, ethyl esters (mainly isoamil acetate), diacetyl, oktalakton in the edges of the threshold concentration have a positive impact on the aroma of rose wines. In small quantities diacetyl can raise "red fruity" flavor that is entirely appropriate for fresh rose. Sulfur-containing components are also responsible for vegetable wine characteristics. They are undesirable elements and their appearance is avoided by selecting of a certain yeast strain [2, 4, 7, 9].

In general the problem of aromatic profile formation of rose wines is very important. At present rose wine sales are second only to white wines, and therefore there is nothing surprising in an increased attention of the scientific community to problems related to the preservation of properties of these wines. That is why the study of the influence of various factors on the formation of the aromatic profile of rose table wines is an actual problem.

The aim of this work was to study the aroma complex of rose table wines that were made of different grape varieties.

The tasks of the research were:

1. To identify the impact of various aromatic components on organoleptic properties of rose table wine.
2. To identify and quantify the aromatic composition of rose table wine.

II. Materials and methods

The objects of research were rose dry wine made of Pinot Noir and Cabernet-Sauvignon that were cultivated in sufficient quantity in Ukraine, with sugar content of 170 and 210 g/dm^3 respectively. The samples were prepared in conditions of micro winemaking by the schemes that included processing without maceration, maceration on mash 3 and 6 hours, mash fermentation to alcohol content by 2% vol.

Fermentation was conducted on pure culture of yeast-killers K-47 selected in NUGaW "Magarach". The mash was treated with sulfite by potassium bisulfite (Döhler company) at doses of 50-75 mg/dm3.

Determination of qualitative and quantitative composition of aromatic complex was determined by gas-liquid chromatography.

III. Results and discussion

After wine preparation an industrial degustation was carried out, the results of it are presented in Table 1.

Table 1. *Organoleptic characteristic of rose table wines made from grapes Pinot Noir and Cabernet-Sauvignon*

№	Name of sample	Organoleptic characteristics	Overall score
1.	Pinot Noir (in white without maceration)	Aroma is bright. Expressed tone of lollipops and strawberries with raspberries.	7,65
2.	Pinot noir (maceration on mash 3 hours)	The aromas of red berries - barberry, strawberry and raspberry. In the latest "nose" - raspberries and cream.	7,8
3.	Pinot noir (maceration on mash 6 hours)	Berry tones in the aroma - red currants, strawberries.	7,8
4.	Pinot noir (fermentation 1 day, 2% vol. alc.)	In flavor barberry, currant and other red berries. There is a faint creamy tone.	7,85
5.	Pinot Noir (in red, fermentation 2 days, 5% vol. alc.)	Flavor berry milk. Good feel raspberries and red currants.	7,7
6.	Cabernet Sauvignon (in white without maceration)	Aroma is not bright, with strawberry tones.	7,5
7.	Cabernet Sauvignon (maceration on mash 3 hours)	Berry aroma, not very developed, with cream and strawberry-raspberry shades.	7,6

Aromatic profiles of samples were received according to the results of the tasting (fig. 1 and 2).

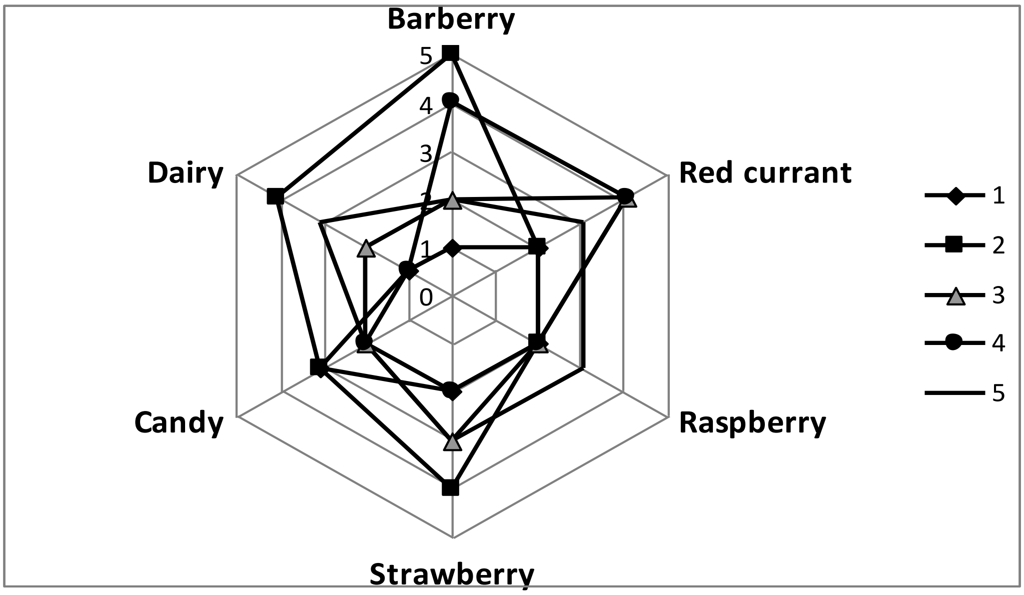

Fig. 1 *Aroma profiles of rose table wines made of Pinot Noir variety*

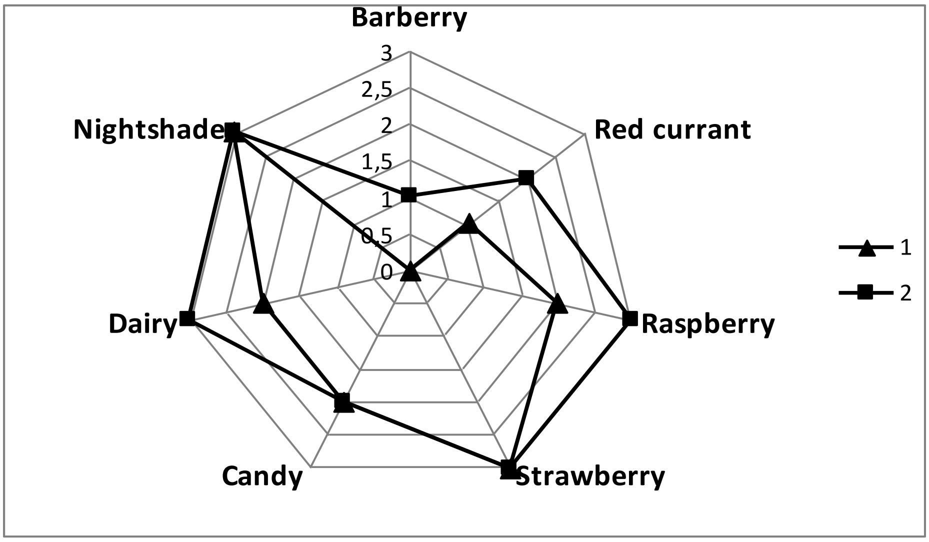

Fig. 2 *Aroma profiles of rose table wines made of Cabernet Sauvignon variety*

The figures show that wines from Pinot Noir have more bright and varied aromas. Then as in wines of Cabernet Sauvignon varietal characteristics started to appear.

The next stage of our research was to determine the qualitative composition and quantitative content of aroma complex of samples.

After receiving the results of chromatography all aromatic components were divided into several groups: higher alcohols, acids, esters, lactones and other components, that include aldehydes, cyclic and aliphatic hydrocarbons saturated and unsaturated character, which were met in small concentrations. (fig. 3).

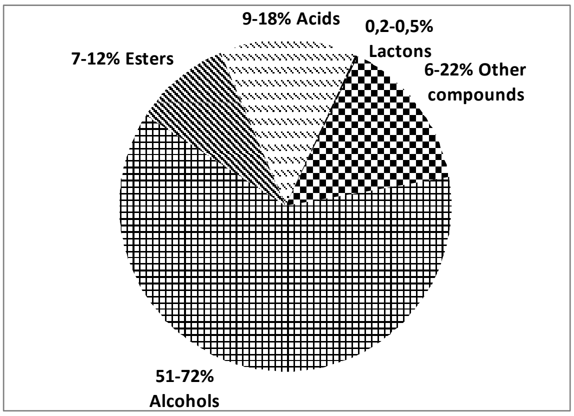

Fig. 3 *Main groups of compounds that form aroma complex of rose table wine made from grapes Pinot Noir and Cabernet-Sauvignon*

As can we see from the diagram, most of aroma compounds are higher alcohols. Of these, about 60-70% of alcohols with short hydrocarbon chain (C1-C5). It is known that alcohols with longer hydrocarbon chain have a pleasant fragrance at low concentrations. Instead, butyl, amyl alcohols and their isomers have very unpleasant odor, but they, along with esters, aldehydes and other components form the so-called "wine background" [4,10]. Main part of higher alcohols in all samples constitutes isoamyl and β-phenylethyl alcohol. The last has a pleasant mild floral scent of roses, hyacinth and honey [1, 7]. His percent in the samples made of Pinot Noir is 12-22 of the total content of higher alcohols, when Cabernet Sauvignon samples contain 28-30%.

Among other alcohols tryptophol, that was measured in high concentrations, has a very unpleasant smell, but at a dilution and combination with other substances it becomes a very nice and pleasant flavor [1, 6]. As well as benzyl alcohol, which has exquisite floral fragrance (its amount correlates with the tasting score with a coefficient of 0.82) [7]. Other alcohols with pleasant aromas that were detected in the experimental samples were hexanol, heptanol, octanol, nonanol, α-bysabolol and tyrozol.

Table 2 shows the mass concentration (mg/dm3) of main alcohols that were detected in the experimental samples.

Table 2. *Mass concentration of higher alcohols in the samples of rose table wine*

№ of sample	Isoamyl alcohol	Isobutyl alcohol	β-phenylethyl alcohol	Tryptophol	Benzyl alcohol	Hexanol
1	210,8	48,5	72,57	1,76	0,17	1,51
2	170,3	41,5	62,26	1,74	0,49	2,38
3	89,7	19,8	53,4	1,19	0,43	1,68
4	105,1	49,5	41,04	0,78	0,85	3,4
5	237,8	92,5	52,82	1,15	0,7	6,7
6	163,5	27,3	99,16	10,26	0,07	1,77
7	145,9	28,5	88,34	9,72	0,1	1,57

Esters made the most diverse group among aromatic compounds that were present in the experimental samples of rose table wine. Although this group constitutes only 7-12% of the total number of aromatic substances, it has a significant influence on the aromatic profile because esters have fairly low threshold concentrations of flavor [2, 3, 4]. Moreover, the esters concentration impacted the tasting score (correlation coefficient 0.83). There were such esters as ethyl acetate, ethyl propionate, butyrate, isoamil acetate, hexil acetate, ethyl caprylate and ethyl capronate whose presence, from written sources, is one of rosé wines markers [2, 4, 7]. It should be also noted the increases in amounts of isoamil acetate, β-phenyl ethyl acetate, ethyl caprylate and ethyl lactate, were observed in samples with higher tasting scores. According to the publications, ethyl lactate concentration in wines can reach 200 mg/dm3, which in turn can lead to an appearance in wine of unpleasant heavy tones [2, 6]. In the experimental samples its quantity was less than 1.8 mg/dm3 and it increased proportionally to an increase in duration of maceration.

As it is known long chain esters have a more pleasant fruity flavor than short chain esters [3, 9]. Cabernet Sauvignon wines were characterized by a wide range of esters, including long chain. For example, a large numbers of esters of caprylic, caproic, lauric, vanillic and succinic acids were detected. All these compounds have pleasant fruity and floral aromas. [9]

Table 3 shows the mass concentration (mg/dm^3) of main esters that were detected in the experimental samples.

Table 3. *Mass concentration of main esters in the experimental samples of rose table wine*

№	Isoamil acetate	β-phenyl ethyl acetate	Ethyl lactate	Ethyl caprylate	Ethyl acetate	Ethyl capronate	Ethyl caprynate	Hexil acetate
1	3,22	4,06	0,71	3,98	14,8	2,1	1,21	0,34
2	17,39	8,65	1,27	5,38	16,4	4,14	0,85	0,99
3	10,4	5,06	1,25	5,29	11,6	2,68	1,19	1,03
4	13,63	6,14	1,7	4,7	11,2	3,5	0,75	0,96
5	9,9	4,14	1,84	3,43	13,2	2,68	0,76	1,49
6	1,12	2,3	0,65	2,39	6,4	0,92	0,99	0,15
7	4	1,95	0,58	2,39	12,8	2,06	0,8	0,16

Along with these unsaturated esters, saturated carboxylic acids were also detected. They have no smell at all or have unpleasant tones. But the threshold of perception of these acids is low, so they do not have a significant effect on the aromatic profile of rose table wines [3, 4].

Butyl lactone was detected in all samples. It has very pleasant smell and appears to be the result of yeast metabolism [2, 7, 10]. Its content varies from 1,1 to 1,73 mg/dm3.

IV. Conclusions

Thus, the results of the research consist in a determining of a group of substances and their representatives that are responsible for the formation of aromatic profile of rose table wines. Among them there are isoamyl β-phenyl ethyl alcohol, hexanol, heptanol, octanol, nonanol, α-bysabolol, tyrozol, ethyl acetate, ethyl propionate, butyrate, isoamil acetate, hexyl acetate, ethyl caprylate, ethyl caprynate, β-phenil ethyl acetate, ethyl lactate and butyr lactone.

These results show directions for a development of the research. An impact of yeast races, fermentation conditions, grape variety and conditions of its cultivation on the formation of the aromatic profile of rose table wines have to be studied.

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ANTIMICROBIAL ACTIVITY OF COTTON OIL OBTAINED FROM NEW BULGARIAN COTTON SEED VARIETIES

M. Perifanova-Nemska, G. Uzunova, D. Blajeva, A. Slavchev

University of Food Technologies Plovdiv
26, Maritza Blvd., 4002 Plovdiv, Bulgaria

Abstract: *The antimicrobial activity of cotton oil of Bulgarian cotton varieties and pure gossypol was studied against Gram-positive and Gram-negative bacteria and yeasts. The glyceride oil, obtained from the Chirpan 539 variety exhibited weak antimicrobial activity against the yeasts Mallassezia furfur and the Gram-positive bacteria in 100 and 1000 ppm concentrations. The investigated cotton oils did not inhibit the growth of the yeasts Candida albicans and the Gram-negative bacteria. Pure gossypol showed high antimicrobial activity against all test-microorganisms in 10 ppm concentrations.*

Keywords: Cotton seed oil, Antimicrobial activity, gossyipol

I. Introduction

Gossypol is a oil soluble pigment. It is located in the gossypol or pigment glands in cotton seeds [4, 10, 19]. It is obtained through press and extraction techniques.

As extraction agents can be used nonpolar and polar diluents, which results in the production of cotton oils with different chemical and physical characteristics.

Extraction oils, obtained from American cotton varieties with traditional diluents (hexane, petroleum ether, diethyl ether) have higher acidity values, phosphatide quantities and gossypol content than the pressed oils, as follows: acidity – 0,814-1,518% oleic acid for oils from gossypol-free seeds and 1,25-5,10 % oleic acid for gossypol seeds; phosphatides (as phosphorus content) – 528-731 ppm; gossypol content – 0,91-1,46% [6, 7, 11, 18].

Gossypol is toxic to people and animals. It is a cell, tissue and nerve poison. It causes inflammatory processes in the tissues, irritation of the mucosal membranes, damage to the heart and kidneys. Due to its solubility in lipids, it is accumulate din nerve cells and causes a variety of inflammatory processes. Up to 0,02 % it is harmless for animals and in 0,02 - 0,2 % concentrations causes severe poisoning [2].

There are reports in reference literature, that gossypol has antioxidant, antibacterial, fungicide and aseptic properties [5, 12, 13, 14, 15, 17]. It protects the cotton plant form insects. Vroh *et al.* [16] determined that gossypol-free cotton seeds were more susceptible to insect infestation. The same authors selected cotton seeds with reduced gossypol content in the seeds, while the content in the other parts of the plant (leaves, roots, stem) were not affected.

Therefore, it is interesting to study the inhibitory effect of oils, produced form Bulgarian cotton varieties and to compare the results to the minimal inhibitory concentrations of pure gossypol.

II. Materials and methods

In the study were used the following materials:

- Cotton seeds from six new Bulgarian varieties from the Cotton and Durum Wheat Research Institute – Chirpan:

- Chirpan 539, ML240, Avangard 264, Beli Iskar 800, Perla 267 and Vega 412 - vintage 2005.

The glyceride oil was obtained through Soxhlet extraction with diethyl ether diluent.

- Pure gossypol, ≥95% (HPLC) (Sigma)
- Test-microorganisms

The used microorganisms from the collection of Department of Microbiology at UFT – Plovdiv, are common causing agents for toxic infections, toxicoses, yeast infections and seborrhea:

- Gram-positive bacteria: *Staphylococcus aureus* ATCC 6538 P

- Gram-negative bacteria :*Escherichia coli* ATCC 8739;

- Yeats:*Candida albicans* ATCC 10234 и *Malassezia furfur* DSMZ 6171.

Analytical methods

- Gossypol was determined according to[3]
- The cotton oils and gossypol were tested in concentration of 100 and 1000 ppm for the oils and 1 and 10 ppm for the gossypol. Control samples without tested substances were used for reference.
- The antimicrobial activity was determined according to the agar dilution method [8, 9], using the test-microorganisms mentioned above in following nutrient media:

- for the bacteria:

LBG (g/dm^3), containing tripton - 10; yeast extract - 5,0; NaCl - 10,0; agar-agar - 15; pH 7,5.

- for the yasts:

Candida albicans ATCC 10234 - Wort agar (Merck),

Malassezia furfur - Medium 472 (DSMZ).

In a 1,5 cm^3 Eppendorf were put 5 μl of a 10 % methylene blue solution, 50 μl of a test-microorganism suspension (viable cell counts were 10^{10} cfu/cm^3), the tested cotton oil concentration and melted and cooled down to 42 °C nutrient medium (up to 1 cm^3). The test tubes were cultivated 37 ºC for 24÷36 h (for bacteria and yeasts). The results were interpreted in the following manner: dark blue colour – the microbial culture is very sensitive and the tested cotton oil has high antimicrobial activity in the tested concentration; light blue colour – the culture is mildly sensitive and the antimicrobial activity is low; lack of blue colour – the microorganisms is not sensitive and there is no antimicrobial activity.

The control sample contained 5 μl of a 10 % methylene blue solution, 50 μl of a test-microorganism suspension (viable cell counts were 10^{10} cfu/cm^3), distilled water and melted and cooled down to 42 °C nutrient medium (up to 1 cm^3). After 36 h at 37 ºC the indicator changed its color to light yellow [9].

The experiments were conducted with five times repetition rate. For statistical data analyses were used Sigma Plot 2008 and Microsoft Excel 2007. During the data analysis was used confidence level α=0.05 [1].

III. Results and discussion

The experimental data shows that the six cotton oils and the pure gossypol have different effect on the growth of the pathogenic and non-pathogenic bacteria and yeasts (Table 1).

Pure gossypol exhibited high antimicrobial activity against all test-microorganisms at minimal inhibitory concentration (MIC) 10 ppm.

The glyceride oils from Chirpan 539 and ML 240 variety seeds showed low antimicrobial activity against the yeasts *Mallassezia furfur* in both tested concentrations (100 и 1000 ppm), and the oil from the Chirpan 539 variety had similar activity against the Gram-positive bacteria. The gossypol content in these oils was 2,71 % and 1,55 %, respectively. The oils from the Avangard 264 and Vega 412 varieties, which had gossypol content of 1,12 % and 1,74 %, inhibited the growth of *Mallssezia furfur* and the Gram-positive bacteria only in 1000 ppm concentrations.

The oils from Beli Iskar and Perla variety seeds did not exhibit antimicrobial activity in the investigated concentrations against all test microorganisms.

None of the investigated cotton oils exhibited antimicrobial activity against the yeasts *Candida albicans* and the Gram-negative bacteria.

Table 1. *Growth in presence of cotton oils and gossypol*

Variety Test-microorganism	Chirpan 539		ML240		Avangard 264		Beli Iskar 800		Perla 267		Vega 412		Pure gossypol	
	100*	1000	100	1000	100	1000	100	1000	100	1000	100	1000	1	10
Candida albicans ATCC 10234	++	++	++	++	++	++	++	++	++	++	++	++	++	-
Malassezia furfur DSMZ 6170	+	+	+	+	++	+	++	++	++	++	++	+	++	-
Staphylococcus aureus ATCC 6538 P	+	+	++	++	++	+	++	++	++	+	++	+	++	-
Escherichia coli ATCC 8739	++	++	++	++	++	++	++	++	++	++	++	++	++	-

*- all concentrations are presented in ppm
Legend:
++ - strong growth of the test-microorganism (lack of antimicrobial activity)
+ - weak growth of the test-microorganism (low antimicrobial activity)
- - lack of growth of the test-microorganism (high antimicrobial activity)

The determined variations in the antimicrobial activity against the same microorganism for the different varieties could be explained with the different gossypol content in them and the interactions between the gossypol and the concomitant substances in the oil (phosphatides, etc.).

IV. Conclusions:

1. The glyceride oil obtained from the Chirpan 539 variety exhibited weak antimicrobial activity against the yeasts *Mallassezia furfur* and the Gram-positive bacteria in both tested concentrations.
2. The investigated cotton oils did not inhibit the growth of the yeasts *Candida albicans* and the Gram-negative bacteria.
3. The pure gossypol showed high antimicrobial activity against the used test-microorganisms at 10 ppm concentrations.

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RESEARCH SMART-PACKAGES WITH ACTIVE PACKAGING SYSTEMS

O. Gavva[1], S. Tokarchuk[2]

[1] Doctor of Technical Science, professor of Technical Mechanics and Packaging Equipment Dept., National University of Food Technologies, Kyiv, Ukraine. E-mail: aleksandrgavva@inbox.ru

[2]Candidate of Technical Science, associate professor of Technical Mechanics and Packaging Equipment Dept., National University of Food Technologies, Kyiv, Ukraine. E-mail: tmipt_xp@ukr.net

Abstract. *In article the results of research "smart-packages" with the active oxygen system scavenging from consumer packaging. Results of research allowed: to pick up the packing material and determine the size of the sachet, in which decreases allocation heat accompanying a chemical reaction oxygen consumption under; the optimal amount of reagent that meets the requirements for the absorption of oxygen in packages with the test food product. The research results can be used to increase the shelf life of food products.*

Key words: oxygen scavengers, iron powder, consumer packaging, active packaging, food

Modern consumer every day more and more requires the manufacturer of new packages and packaging materials, which not only would not only protect the packaged products from physical, chemical and biological processes, but also to be effective and easy to use. Manufacturers, in turn, try to keep up with the needs of consumers. One of the new types of packages, which are gradually emerging and gaining a place in the food products are «smart-package" with the use of active packaging systems.

The notion of «Smart-package" consider new types of packages, which include the "active" and "intelligent" packaging, as well as functional components for the creation of "smart" packaging design. Introduction of «Smart-packages" using active packaging systems covers all aspects of the use of advanced packaging materials, and the introduction of mechanical and chemical components, or a combination thereof, extending the shelf life of food products while maintaining their qualitative and quantitative characteristics.

One of the first places in the world among of packaging materials used for food packaging is confidently occupy polymer films. Analysis of existing methods extend the shelf life of food products packed in polymeric film package shows that gained widespread use vacuum packaging and use of modified atmosphere (MAP). Like any other ways to extend the shelf life of foods they have a number of advantages and disadvantages.

Packing in MAP is a way of packing, in which air is removed from the package and replaced with a gas or gas mixture. Gas mixture is selected depending on the type of product (usually the air is replaced with nitrogen and carbon dioxide). Gases are not deformed and not compressed products, that is very important for packaging of many meat products, fresh bread, ready meals, convenience foods and etc. During the period of storage of the product gaseous atmosphere inside the package is constantly changing. This is due to factors such as the "breath" of packaged products (oxygen consumption and carbon dioxide emissions), biochemical changes in the product and the associated allocation of vapors and gases, and the gradual penetration of the head space of atmospheric gases and vapors through the walls of the package and through pinholes in the welds. Oxygen, which is in the package, allows you to preserve the freshness and natural color of chilled meat, prevent botulism of fish products, as well as support the process of "breathing" for fruits and vegetables, and, conversely, inhibit the growth of anaerobic organisms in some types of fish and vegetables. But, in turn, he is the originator of oxidation and rancidity of fats, food spoilage as a result of the growth of aerobic bacteria. On the other hand, without him can not do, if you want to, for example, to keep a bright red color of beef, which is associated by consumers with its freshness. One way to address these concerns in the process of food storage is the targeted impact on the MAP.

Due to the problems that occur during storage of raw materials, food products and semi-finished products in the MAP, the active development of the concept becomes larger storage stability by controlling and regulating the composition of the gas in the package using the «smart-packs" with a self-regulating and actively controlled atmosphere. Active packagings call type of packaging, components or materials that change their properties to protect the product, increasing the shelf life of the goods [1]. The main function of "active packaging" is the targeted impact by the product or the internal environment of the packaging for long-term storage of its quality, as well as to extend the stability and availability [8]. Technologies associated with "active packaging" expanded function from passive packaging barrier relative to the external exposure to the active product protection [2]. The principle of "active" control of the atmosphere founded on the absorption and emission of gases in the package.

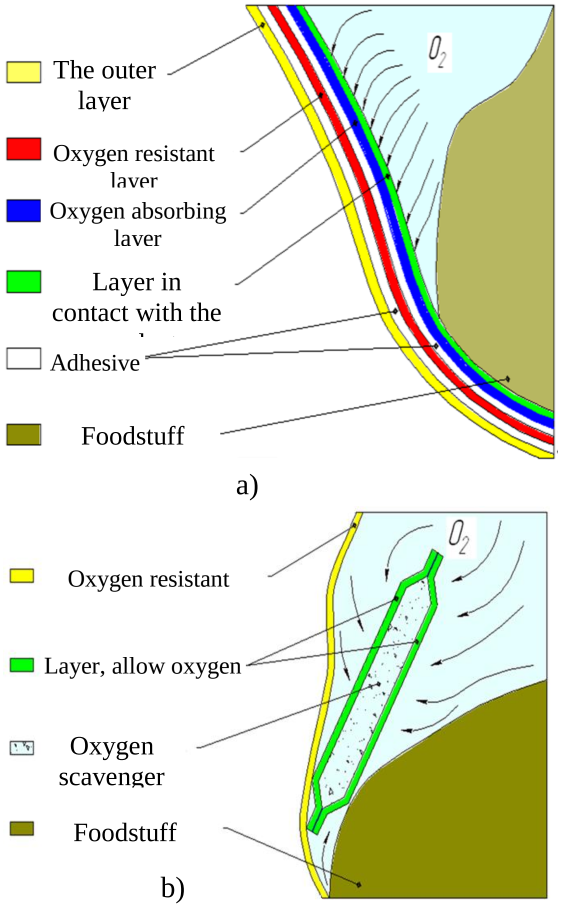

Fig.1. *The design of packages: a) with active oxygen absorbing layer b) with the sorbent, which is located in the sachet.*

This provides meaningful regulation of the atmospheric environment in the package due to the chemical or enzymatic removal of unwanted gases [4]. Absorption, with a specially selected sorbent be all residual oxygen, which is in the package at the time of sealed and flow through the film during storage. In this case persist, as close as possible to the initial, parameters such as taste, smell, color and consistency of many perishable foods. This is what contributes to the reduction of growth of aerobic microorganisms [6].

Existing packaging systems controlling the amount of oxygen is conventionally divided into two types - with oxygen scavenger layer in the package design or with the sorbent-oxygen scavenger, which is located in a special envelope (Fig. 1). As oxygen scavengers use substances that can be chemically or enzymatically remove oxygen, which will provide product protection and preservation of its quality.

Representatives of sorbents - iron oxide (iron powder), ascorbic acid, iron-salt powder, mixture of iron oxide and potassium chloride, calcium etc. Polymers such as nylon fibers ducted cobalt MXD 6, can be used as an oxygen-absorbing layer inside bottles of polyester. Other systems may be based on the absorption of unsaturated polymers, such as 1, 2-polybutadiene [3, 5]. The use of multilayer polymer films with active oxygen scavenger layer for the packaging of food is limited. This is due to the incompleteness of scientific research in the field of their application for the packaging industry and the likelihood of contact is the chemical reaction of oxidation and food. Most manufacturers prefer to use when packing the sorbent, which is placed in a special envelope - package. However, it also raises a number of specific issues to be addressed, namely, what kind of packaging material used for the production of packages, because it should provide the penetration of oxygen to the sorbent and hold inside the shell products of the chemical reaction; how many of reactant must placed in the package for effective oxygen consumption; what should be the geometric parameters of the package with the sorbent.

That is why the purpose of the research was the choice of packaging material, the geometric dimensions of containers for oxygen scavengers, as well as quantification of the reactant necessary for the chemical reaction of oxidation of the sorbent and the absorption of oxygen. As the oxygen scavenger were elected packages-sachet (Fig. 1.b) which are packaged in the consumer packaging. The choice of this method of controlling the gas atmosphere in the package based for simplicity and high efficiency. As a sorbent-scavenger oxygen was elected iron oxide as one of the most common materials for absorbing. Object of research were plastic packaging with dried meat, production company "Drayd Fudz" (Ukraine). To determine the efficiency of oxygen scavengers, which are packaged in a variety of packaging materials, was used analyzer brand OpTech-O2 Platinum (Fig. 2).

As a research of packaging materials were chosen: EVA film - (20mkm), low density polyethylene - LDPE (20mkm) and films Ecolean with various impurities Ca (15 mkm). Focusing on the production of "Drayd Fudz" were made the packages-sachet.

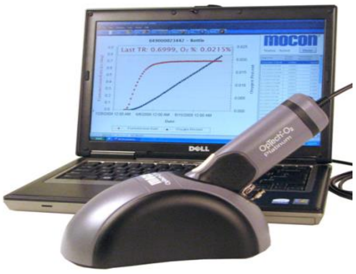

Fig.2. *Gas analyzer brand OpTech-O2*

In the ready package was placed 4 grams of iron powder and 0.6 ml of water, after which he was closed and placed in a package with food. The next step was to seal the consumer packaging. For dried meat need of the oxygen concentration in the consumer pack over 48 hours was less than 0.1% [7]. On the basis of this condition, the duration of the measurement cycle was 48 hours; the kinetics of the absorption oxygen in each of the packages was measured every 4 hours.

Results are presented in Fig. 3.

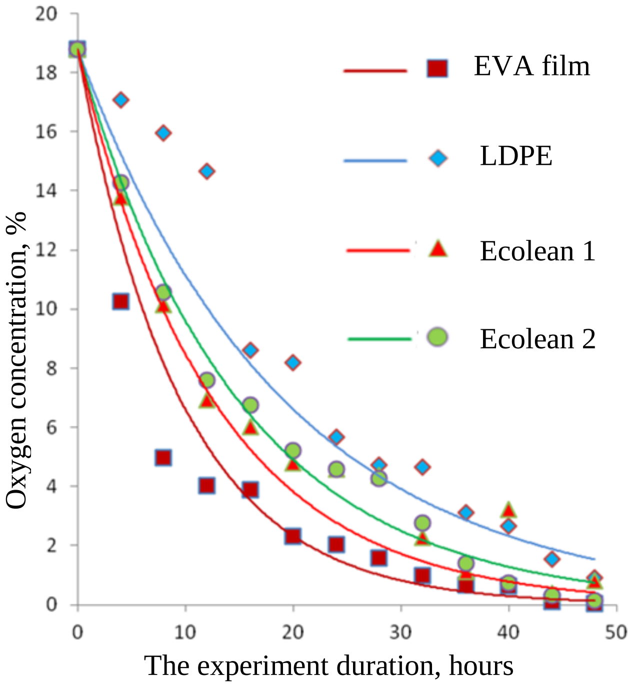

Fig.3. *Chart of absorption package-sachet.*

This diagram shows that the intensity of the absorption of oxygen decreases with time; she is accompanied by a decrease in the degree of oxidation. The highest gas permeability of packaging materials was at the EVA film with a thickness of 20 microns.

To determine the efficiency of oxygen consumption in the consumer packaging with food (meat snacks) were made bags-sachets with different amounts of water in the structure of an oxygen scavenger. As a packaging material was used film of EVA, with a thickness of 20 microns. Amount of Water for 4 grams of iron powder was respectively 0,2; 0,6 and 1,0 ml. To process the measurement results was necessary to define the regularities of variation of oxygen consumption for the period of time equal to 48 hours for each oxygen scavengers with different moisture content

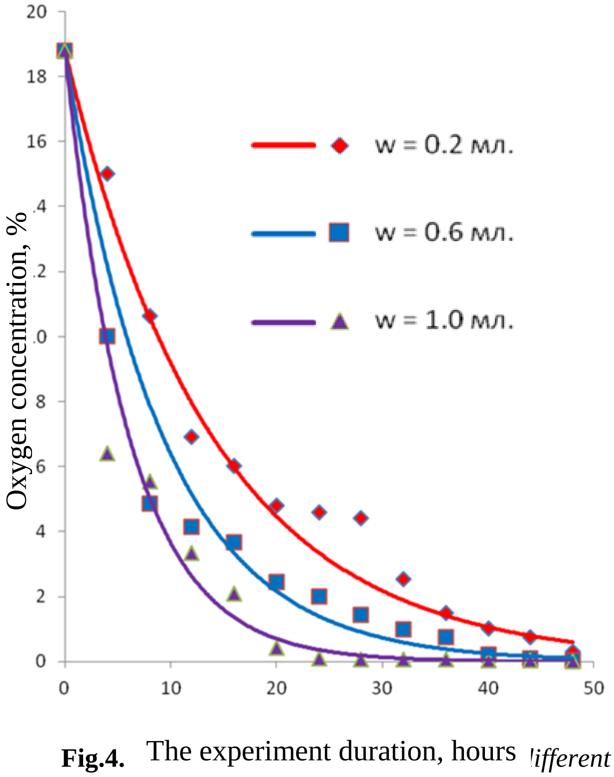

Fig.4. *ifferent moisture content in the packages-sachet*

The results are shown on Fig. 4.

This diagram shows that the intensity of the absorption of oxygen decreases with time; it is accompanied by a decrease in the degree of oxidation. Effectively works oxygen scavenger with the amount of water 1,0 ml. which for 24 hours absorbs the oxygen before concentration 0,01%. At the same time, with such intensity absorption is allocated significant amounts of heat, which does not meet the requirements established by the manufacturer with respect to the tested product. Oxygen scavenger with 0,2 ml of water works inefficient, as it is not consumed the right amount of oxygen for 48 hours; only the oxygen scavenger with 0,6 ml of water fully complies with established requirements.

For the selection of the most efficient geometric dimensions of sachets with oxygen absorbers were examined three variants of the size sachets: 10x15 mm., 20x30 mm., 40x60 mm.

The results are shown in Fig. 5.

The diagrams show that the intensity of the absorption of oxygen decreases with time; it is accompanied by a decrease in the degree of oxidation. Most efficiently works oxygen scavenger in the sachets with the geometric dimensions 40x60 mm., but absorption of oxygen passes with a temperature of 32 ° C, which leads to heat the food and the loss of quality. Oxygen scavenger with dimensions 10x15 mm. showed the lowest absorption efficiency because its effective area was smallest. Oxygen scavenger per sachet with dimensions 20x30mm., as seen from the diagram (Fig. 5.) for 48 hours reduced the oxygen concentration to 0.05%, which fully meets the requirements of the manufacturer.

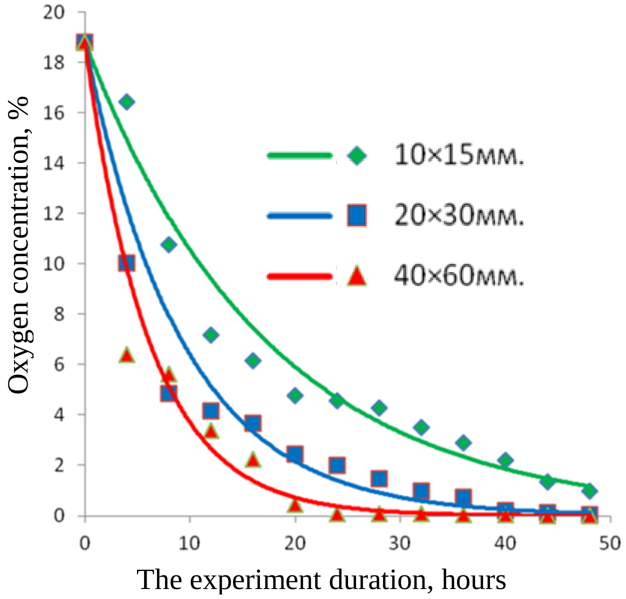

Fig.5. *Diagram of oxygen absorption with packages-sachet different sizes*

Output. The research led to the development of plastic packaging for oxygen scavengers. Was chosen packaging material (EVA film with thickness 20 micron), allowing the absorb oxygen from the interior of the consumer packaging for food product. Also identified the oxygen scavenger, at which the decreases heat during the chemical oxidation of iron powder. It was determined the optimal number of the reactant, which came to a chemical reaction of oxidation of iron powder and provide of the requirements for the absorption of oxygen in the test food product.

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DEVELOPMENT OF FOODSTUFF OF THE DIRECTED ACTION ON THE BASIS OF NATIONAL CUTTING OF MUTTON

L. Baibolova[1], T. Kulazhanov[1], B. Rskeldiev[2],
K. Baibolov[3], S. Dzhinguilbayev[1],
K. Tutebayeva[1], A. Kemerbekova[4], A. Admayeva[1]

[1] Almaty technological university, str. Tole bi, 100, Almaty, 050012, Kazakhstan, e-mail:
baybolova@mail.ru,
[2] Semipalatinsk State University named after Shakarima, str. Glinki, 20 A, Semey, 071412, Kazakhstan,
e-mail: berdan_r@mail.ru
[3] LLP «SEZAM ECO», Office 206, Business Center "Munayshi", Str. Amangueldi, 49A, Almaty,
Kazakhstan, Candidate of Engineering Science,
e-mail: nfo@sesameco.kz
[4] LLP «Engineering Regulation and Metrology Center», Str. Mametovoy, 36/38, Almaty, 050004,
Kazakhstan, e-mail: kemerbekova.kz@mail.ru

Abstract. *In the article the research findings as to the national cutting and separation of meat for Kazakh national meat products production are introduced.*

Key words: meat products assortment, fresh meat, national dressing, mutton, horse meat

I. Introduction

The stabilization of economic progress, extension of the market relations of modern Kazakhstan, cattle herd expansion cause the development of the meat industry of the republic. At the same time over the last years at the domestic market there has been the tendency of import growth for the meat and meat productions (up to 64 %).

There is the problem that the meat factories of the republic are behindhand in assimilation of the innovation technologies and technological infrastructure.

However, in Kazakhstan meat is consumed more than it is produced. If the demand for meat in 2010 made 1252,9 thousand tons, in 2011 – 1560,5 thousand tons, in 2012 – 1923,5 thousand tons, it makes 16 % increase on the average.

In modern times the matters of the market saturation with the meat products of domestic production, improvement in quality, competitive growth, and assortment extension take an enormous significance. We have the backgrounds for this – this is a steady annual growth of the cattle head, increase in its efficiency and volumes of meat production. In 2012 in comparison with the level of 2010 the production volumes gave 19,5 % increase. The potentialities of the agricultural sector of the country allow providing with the agro food security for such production and entirely satisfying the domestic consumer demand of the population.

However, the assortment of specialty food, made of mutton, offered by the producers, is a little bit limited, the meat products with the domestic functional purpose are almost not produced, though the scientists and specialists make significant and rather successful developments in this regard [1].

To solve the above problems we propose:

- the efficient use of the domestic fresh meat;
- filling in of the domestic market with the wide assortment of meat products of the domestic producing;
- development and implementation of the products created before and now, taking into account all the requirements of the functional nutrition of the meat products with intended end-use;
- up-grading and improving the efficiency of work of the current productions and creating of the new high-technology productions, export oriented;
- competitive growth for the product.

The mutton is one of the main kinds of fresh meat in Republic of Kazakhstan. Nowadays in the Republic the market share of the mutton is about 25 % of all the meat, produced in the country.

Nowadays, according to Professor's Uzakov Y.M. data, practically the whole volume of the mutton produced is realized in the carcass and in half carcass directly to the population. The wide use of the mutton is observed in the system of public catering system for cooking the meal and ready-cooked foods.

The mutton is used for producing the canned food, as well as some sausage ready-cooked foods. However, such use is limited during the inter-season and only when there is a lack of other fresh meat [2].

II. Materials and methods

1.1. Raw and materials

Food maintenance of the population of Republic Kazakhstan with high-quality, ecologically safe foodstuff concerns one of the most priority scientific and technical, economic and social problems solved at the state level.

The mutton of meat bread of the 1-st and 2-nd category, pumpkin, sesame, peanut and caraway seed oils, the standard methods for chemical, physicochemical, fatty-acid, vitamin and mineral substances composition analysis.

1.2. Methods of researches

The combination of traditional and advanced processing methods of processing and preparation of agricultural raw materials in a complex with modern methods of the analysis of the data will allow to receive products with high food advantages and to raise efficiency of production cycles.

For achievement of objects in view of the article and a substantiation of the scientific approach applied methods of researches owing to the specific directions for convenience of conducting research works have been united to signs and prominent features in mentioned below groups: 1. Physical and chemical methods of researches, 2 Biochemical methods of research, 3 Medical and biologic methods of researches, 4 Microbiological methods of research, 5 Histologic methods of researches, 6 Methods of computer designing.

1.3. Used equipment

Centrifuges terrify case, an autoclave, a distiller, a microscope, fotoelektrokolorimeter, chromatography, spectrophotometer, scales, etc. In work will system processing methods on preparation and processing of agricultural raw materials, creation of food additives, laboratory, biochemical and statistical methods of research are used.

III. Results and discussion

In accordance with the findings of the scientific research, carried out together with the colleagues of the specialized department «Foods technology» of the University of Technology, the possibility of multipurpose utilization of the mutton carcass has been determined. At that, the raw material was separated for its further processing with the loss test. Also the method of the national cutting of mutton (Kazakh-styled) is kept up to date – along the joints (zhilikteu). The difference of the proposed method from the traditional dressing is that the sheep carcass dressing is fulfilled along the joints without deboning, in other words, without further dissection of the raw material that prevents the meat from a contact with the pieces of bones.

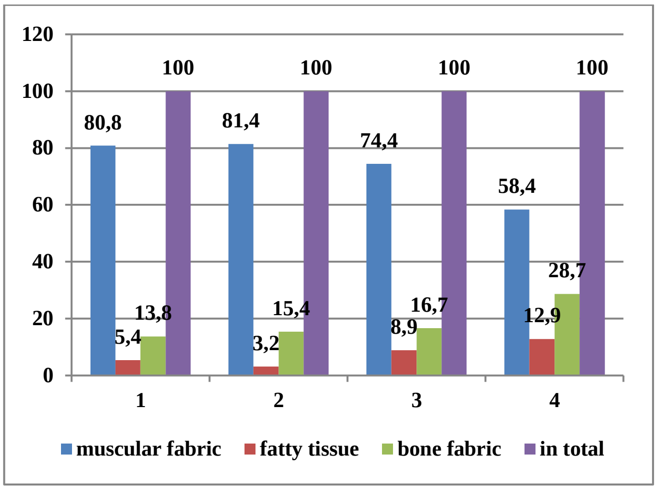
The output of the raw material made of the mutton, nourished under the 1-st category, for the shoulder (zhauirin) makes 20,69 %, back side (zhambas – a round, hucklebone of a mutton that is offered boiled to the guest of honor separately) – 30,27 %, a lumber part (beldeme) – 7,56 %, a neck (moyin) – 5,36 %, sube – 9,28% (Table 1).

Table 1. *Results of the 1-st category mutton cutting Kazakh-styled*

№	Name of cutoff	Output, kg	Percentage, %
1	2	3	4
1	**Components:** **Shoulder**	5,55	20,69
2	**Tag**	8,12	30,27
3	**Beldeme**	2,07	7,56
4	**Thick dock**	1,70	6,34
5	**Moyin**	1,44	5,36
6	Backbone	2,05	7,64
7	**Loin – Sube** **including: ribs – kabirga**	2,49 1,05	9,28 3,91
8	**Asikti zhilik – Hock bone**	0,82	3,06
9	**Brisket**	0,87	3,24
10	**Kidneys with suet**	0,66	2,46
11	**Trimmings meat**	0,80	2,98
12	**Tendons and soft tendons**	0,08	0,30
13	**Technical trimming and losses**	0,17	0,63
	Total	**26,82**	**100**

At that, for the production of the sausage production made of mutton of the 1-st category makes 18,49 kg (68,9 %), the 2-nd category – 14,58 kg (65,71 %), and the most essential parts of a carcass used in the production of national products make: zhambas of the 1-st category 6,12 kg (22,82 %), of the 2-nd category 5,82 kg (26,23 %) and zhauirin of the 1-st category 2,21 kg (8,24 %) and of the 2-nd category– 1,79 kg (8,06 %). The chemical composition analysis of the trimmed mutton of meat breed nourished under the 1-st and 2-nd categories according to the sorts under the current and experienced schemes specified that the most nourishing as to the content of the native protein, is a short rack, ramp and tag of the mutton carcasses.

On purpose to find out the nutrition value of the particular cuts-off, the tests were conducted to determine the morphological composition of the mutton carcass of the meat breed nourished under the first category. The test findings are shown in Figure 1.



1 – zhambas, 2 – zhauirin, 3 – sube, 4 – beldame

Figure 1. *Morphological composition for particular the 1-st category mutton carcass cut-offs, %*

The soft part «zhambas» and «sube» is characterized by a muscular surface fat layer, and the reduced quantity of chains improves the cooking and food characteristics of such parts.

In practice, «beldeme» and «moyin» are used in public catering and domiciliary only for broths to be cooked. This is the only usage of these parts in cooking. These parts have a little bit more bone tissue and less muscular, but the food characteristics are almost equal with other parts in the complex correlation. Also «beldeme» and «moyin» are of a great interest nation-wide, because they meet the Kazakh traditions of representing and servicing of the part of mutton carcass in a dish as a traditional food (Attachment 1). The production output when the mutton is dissected and trimmed (as a percentage of the meat with bones mass) is shown in Figure 1a and 1b.

The data analysis insures that, when the mutton is dressed Kazakh-styled, the output of the trimmed meat and slaughter fat show 9,3 % increase in comparison with the traditional dressing. The output of bone, connective, cartilaginous tissue, technological trimming and losses decrease. At that, the raw material output for the national prefabricated meat increases two-three folds in comparison with the retail sheep dressing.

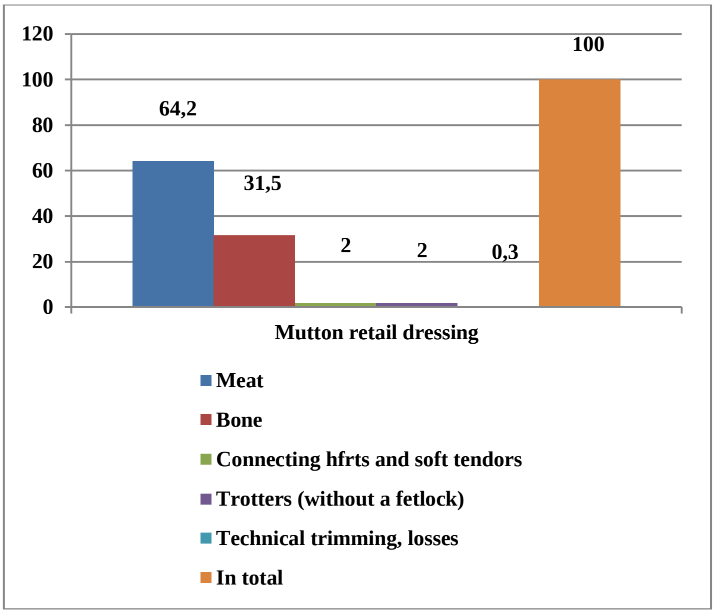


Figure 2a. *Output of production when the 1-st category mutton is dressed in retail*

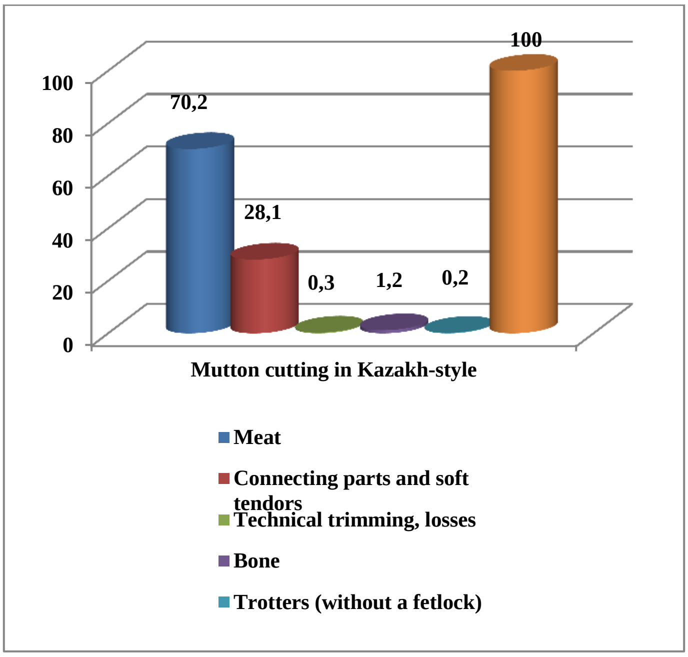


Figure 2b. *Output of production when the 1-st category mutton is dressed Kazakh-styled*

In practice, unfortunately, «beldame» and «moyin» are used in public catering and domiciliary only for broths to be cooked. This is the only usage of these parts in cooking. These parts have a little bit more bone tissue and less muscular, but the food characteristics are almost equal with other parts in the complex correlation. Also these parts are of a great interest nation-wide, because they meet the Kazakh traditions of representing and servicing of the part of mutton carcass in a dish as a traditional food [3].

According to the organoleptic indicator it was determined that the mutton carcasses, chosen as a test subject, have a well-developed muscles, bones emerge slightly, fat deposit are observed around hipbones, outside round, on belly wall, between the muscle groups of hip, rack, chest, near kidneys there are the limited fat deposits, there is a thick dock in the mutton carcasses. The color of the muscle tissue is pale pink for the mutton, the fat is milky-white. The muscle fibers are thin; have fine granular structure inside. The consistence of the muscle tissue is elastic, of the fat tissue is soft.

For the production of meat products with directed effect we used the following raw material: trimmed horse meat, trimmed mutton, food salt, sand sugar, spices, protein-fatty emulsion (PFE) that consists of: the 1-st variant caraway oil, pumpkin oil, soybean isolate, the 2-nd variant pumpkin oil, pumpkin oil, soybean isolate, the 3-rd variant peanut oil, pumpkin oil, soybean isolate.

At the first stage of the test the analysis of the pumpkin, sesame, peanut and caraway oils was carried out. In Table 2 the quality performances for the oils, used in bioactive additives (BAA), are shown.

Table 2. *Quality performances of BAA oils*

№№	Name of performance	Norm	Pumpkin oil	Peanut oil	Caraway oil	Sesame oil
1	2	3	4	5	6	7
	Physic-chemical characteristics					
1.	**Damp, %**	Not more than 0,15	0,065	0,055	0,2	0,07
2.	**Color value, mg iodine**	Not more than: 35-55	35-55	45-55	45-55	35-55
3.	**Acid value, mg КОН/g**	Not more than: 4,0	2,0	0,9	4,2	2,7
4.	**Refraction index under 20 °С**	1,468-1,472	1,4715	1,4716	1,472	1,472
5.	**Saponification value, mg КОН/g:**	Not more than 188-189	188-198	188-198	188-189	188-198
6.	**Density under 20 °С, g/sm3**	911-929	0,915-0,925	0,915	0,915	0,918
1	2	3	4	5	6	7
7.	**Peroxide value, mM O2/kg**	10,0	10,0	10,0	9,7	4,8
8.	**Iodine value, g I2/100 g:**	100-110	100-110	108-110	105-108	100-110
9.	**Weight fraction of unsaponifiables, %**	Not more than 1,0	1,0	1,0	1,0	1,0
	Fatty-acid composition					
10.	**$C_{16:0}$ Palmitic**	8,3-16,0	5,8	9,00	15,36	7,24
11.	**$C_{16:1}$ Palmitoleic**	Up to 1,0	0,02	0,21	0,91	0,29
12.	**$C_{18:0}$ Stearic**	1,9-7,1	4,9	2,67	3,31	7,04
13.	**$C_{18:1}$ Olein**	36,4-67,1	28,4	36,92	24,29	41,75
14.	**$C_{18:2}$ Linolic**	14,0-73,0	20,7	51,04	55,99	43,05
15.	**$C_{18:3}$ Linolenic**	Up to 1,0	0,57	0,13	0,14	0,63
16.	**Saturated fatty acid**	-	12,28	11,77	18,67	14,28
17.	**Monosaturated fatty acid**	-	27,90	37,13	25,20	42,04
18.	**Polyunsaturated fatty acid**	-	59,82	51,10	56,13	43,68
19.	**In total fatty acid**	-	100,0	100,0	100,0	100,0
	Vitamins					
20.	**E, mg,%**	-	34,3	35,5	31,2	36,3
	Microelements					
21.	**Zink/Calcium, mg**	-	8-10/-	-	/9,6-12	-
22.	**Magnesium, mg**	-	3-4	-	-	-
23.	**Ferum, mg**	-	13-15	0,9-1,0	10-12	0,5-0,6

As seen in Table 2 the quality performances for the oils, used in BAA as a raw material, have no deviations, especially physicochemical ones, what bears evidence of their high technological and therapeutic characteristics.

The use of BAA has a favorable impact on the structural characteristics of meat products. The plasticity of the samples increases from $3{,}45\cdot10^2$ m^2/kg to $4{,}24\cdot10^2$ m^2/kg during 48 hours, then in the course of time it changes slightly. If it is processed mechanically, the plasticity increases by (8-9) %. The cut-off stress test supports the tendency as to a change of the plasticity of meat. So, in the salt products made of horse meat the cut-off stress decreases from 420 kPa to 170 kPa, at that, the mechanical processing results in more sharp decrease of the cut-off stress performance.

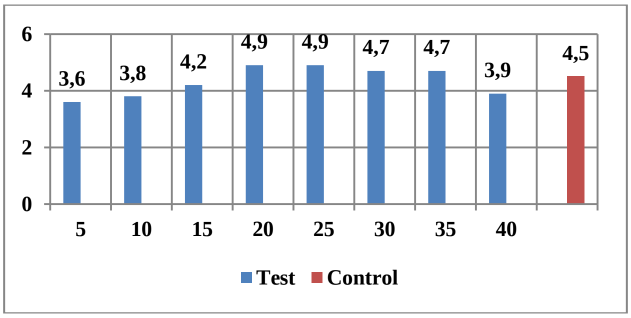


Figure 3. *Organoleptic estimate of experienced samples*

For the purpose of estimating of the quality of the final products to the full extent, the organoleptic analysis of the developed samples is carried out – Figure 3.

It is shown that the final products (the share of BAA is 15-20 %) in comparison with the control sample (Assessment 4,5) have the high flavoring characteristics and estimated by the tasters of ATU as the products of very good quality – Attachment 1.

IV. Conclusions

So, the conducted tests allow making conclusions:

1. the national method of the mutton dressing (zhilikteu) mitigates the loss and increases the output of joints;
2. the parts of mutton, horse meat, separated by such method, are used in production of the national products that expands the assortment for the domestic consumer with meat products of intended end-use, and increase competitiveness of the national products of domestic producing;
3. the quality performances, which characterize the nourishing value of BAA, say that there is a significant quantity of carbohydrates and protein, balanced with all the essential amino acids, at that their quantity meets the requirements of FAO/WHO and equivalent to standard protein;
4. the experienced samples of the product according to their organoleptic performances or characteristics are determined by the testers of ATУ as the direct effect products with high quality characteristics.

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Attachment 1

Zhanbas – a hucklebone of mutton that is offered boiled to the guest of honor separately

Beldeme – a lumber part

Moyin – a neck

Assortment of national Kazakh products made of mutton

PRODUCTIVITY AND EXPANSION INDEX OF CORN EXTRUDATES WITH A FILLING

Ap. Simitchiev[1], Nenov V.[2]

[1]*PhD student, engineer, department MAFP, University of Food Technologies Plovdiv,*
26, Maritza Blvd., 4002 Plovdiv, e-mail: asimitchiev@mail.bg.
[2]*Associate Professor, Dr., engineer, department MAFP, University of Food Technologies Plovdiv,*
26, Maritza Blvd., 4002 Plovdiv, e- mail:vnenov2001@yahoo.co.uk, tel. 0889457286.

Abstract: *A coextrusion die with submission of the filling mass perpendicular to the axis of the extruder is designed and constructed. It is suitable with the laboratory extruder "Brabender" 20 DN. A corn semolina with fat-based filling are extruded with the die. The authors implemented a multi-factorial experimental study for creation of mathematical regression models, linking the independent variables that affect the productivity and the expansion index of corn coextrudates with a filling.*

Keywords: extrusion, coextrusion, rheology, fill.

I. Introduction

The coextrusion of food products is an original method that enrich the range of bakeries with filling and coating. The method consists of uniting two products with different nature such as hard based cereal tube and a high-viscosity product, serving as a filler.

In technical literature and scientific journals the information about the coextrusion process is highly based on the operating principles. There is a wealth of information in the patent offices about the different forming dies, machines and mechanisms. There is no information about the technological regimes, the requirements for the individual components and technological equipment (Velchev et.al., 1988; Nenov et.al., 2003), which is a prerequisite for the detailed study on the problem.

As a technical and economic indicators of the process appear: productivity, torque, consumption of specific mechanical energy and expansion index. As a basis for assessing the quality of the coextrudates appear the organoleptic indicators, some of which are directly related to their physical and mechanical properties. The expansion ratio is considered as a quality indicator. It's one of the most important properties of the food products, obtained at high temperatures and low moisture. The expansion index is an important indicator of the final product crunchy texture (Patil et.al., 2007).

The process productivity (mass flow) is a major feasibility parameter that characterizes the work of the extruder. In single-screw extruders, it mostly depends on the rotation frequency of the working screw, the design of the die and the created pressure (Mercier et.al., 1975, Rosentrater et.al., 2009).

II. Materials and methods

A coextrusion die with submission of the filling mass perpendicular to the axis of the extruder is designed and constructed. It is suitable with the laboratory extruder "Brabender" 20 DN. With this die, the outer shape (the pipe) is fed to the extruder axis, and the filling is fed perpendicular to the axis. The coextrusion die consists of sleeve 7, which is connected to the body 5 through bolting. The die joins the extruder through the union nut 6. The material forming the tube, enters the body through the hole A, passes through the sleeve 7 and the body 5 and reach the needle 4. Going through the five frontal holes it enters the tapered bore of the nut 2 and exit outside of the die through the hole B of the molding nozlle 1. The filling is submitted through the laboratory stand for regulated submission of a filling mass (Nenov et.al., 2012) and pass through the nipple 3 which is connected by a bolting with the needle 4. After joining the tubular portion of the needle it exits through the hole B which is concentric to the nozzle 1.

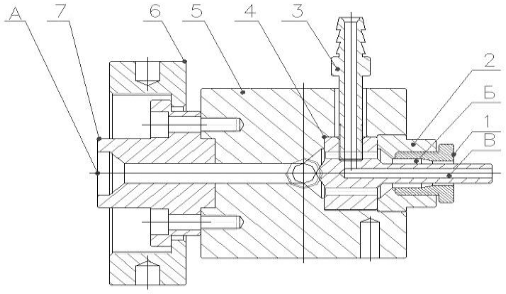

Fig. 1. *Coextrusion die with submission of the filling mass perpendicular to the axis of the extruder. 1.Nozzle 2.Lever nut 3.Nipple 4.Needle 5.Body 6. Union nut 7.Sleeve.*

Corn semolina with an average particle diameter d=1,138 mm is used for the formation of the outer casing pipe. Fat-based fill "cocoa" is used as a filling mass.

The productivity of the process is determined by calculating the mass amount of product expired per time unit at the equation:

$$Q_{ср} = \frac{m}{t}, \text{ kg/h} \qquad (1),$$

where m- mass of the coextruded product, kg; t- time, min.

The transverse expansion index is calculated by the equation:

$$EI = \frac{D_e^2 - d_e^2}{D^2 - d^2} \qquad (2),$$

where D_e and d_e – outer and inner diameter of the coextrudate, mm; D and d – inner diameter of the nozzle and outer diameter of the needle, mm.

The major goal of the study is the implementation of a multi-factorial experimental study for creation of mathematical regression models, linking the independent variables that affect the productivity and the expansion index of corn coextrudates with a filling.

III. Results and discussions

The following independent variables are selected after the preliminary experiments: rotation frequency of the lobes pump $n_п$, min^{-1}, innner nozzle diameter (D, mm) and rotation frequency of the extruder working screw ($n_{раб,}$ min^{-1}). Full factorial experiments of the type 2^3 is used to examine the influence of the selected independent variables on the productivity of the process and the expansion index of the coextrudates. Constant parametres during the experiments are as follows:

1. External diameter of the needle d=8mm,
2. Temperature in the three zones of the extruder $t_1=165^oC$, $t_2=185^oC$, $t_3=190^oC$,
3. Compression ratio of the screw K=5:1,
4. Rotation frequency of the dosing screw $n_{доз}=40min^{-1}$,
5. Average moisture of the corn semolina W=12,8%,
6. Temperature of the filling mass $t_k=45^oC$.

Table 1. *Levels and ranges of variation of the independent variables*

Independent variables	**High level** $Z_j^Г (X_j^Г)$	**Low level** $Z_j^Д (X_j^Д)$	**Center level** $\bar{Z}_j$	**Range of variation** ΔZ_j
Rotation frequency of the lobes pump (X_1, min^{-1}) [Factor A]	31,7 (+1)	21 (-1)	26,35 (0)	5,35
Inner diameter of the nozzle (X_2,mm) [Factor B]	10 (+1)	9 (-1)	9,5 (0)	0,5
Rotation frequency of the working screw (X_3,min^{-1}) [Factor C]	200 (+1)	160 (-1)	180 (0)	20

The matrix for the experiment planning in encrypted form and the results from the experiments are shown on table 2. The results are obtained on the basis of threefold repetition.

Table 2. *Plan of the experiment in encrypted form and results from the experiments*

№	X_1, min^{-1}	$X_{2,}$ mm	X_3, min^{-1}	Q, kg/h			$Q_{ср}$, kg/h	EI			$EI_{ср}$
				1	2	3		1	2	3	
1	-	-	-	14,8	14,25	14,64	14,58	18,03	17,64	18,0	17,90
2	+	-	-	18,0	17,68	18,02	17,93	17,6	17,03	17,1	17,26
3	-	+	-	24	24,18	23,96	24,05	7,94	8,15	7,74	7,94
4	+	+	-	30,9	30,66	29,82	30,47	7,86	7,72	8,04	7,87
5	-	-	+	18,2	18,02	18,25	18,18	13,7	12,9	12,7	13,12
6	+	-	+	22,4	22,12	22,28	22,28	11,39	11,98	12,0	11,82
7	-	+	+	28,0	27,56	27,52	27,72	6,82	7,2	7,12	7,05
8	+	+	+	34,5	34,72	34,62	34,63	7	6,92	7,1	7,01

Productivity

The results from the experiments show that the highest productivity (34,63 kg/h) occurs in the higher levels of the independent variables, and the lowest (14,58 kg/h) when all variables are at their lower levels. The R-squared coefficient is R^2=99,87%, thus the obtained regression model (equation 1) describes a high precision research process.

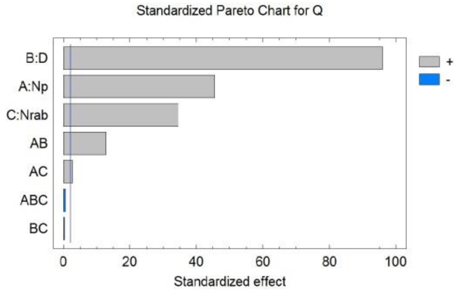

Fig.2. *Pareto chart for productivity*

The Pareto chart (fig.2) show that the change in the inner diameter of the nozzle is the most significant factor that affect the researched process.

The diagram for the distribution of the residual values of the regression model is presented on fig.3. It show that the residuals are equally distributed around the zero line, and there aren't values that surpass the standard error value.

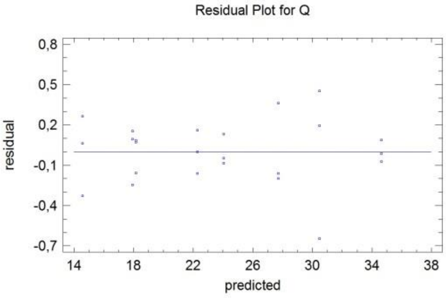

Fig.3. *Residual distribution diagram for productivity*

After processing the experimental results and elimination of the insignificant factors the following regression model is obtained:

$$Q_1 = 23{,}73 + 2{,}6X_1 + 5{,}49X_2 + 1{,}97X_3 + 0{,}735X_1X_2 + 0{,}16X_1X_3, \text{kg/h}. \quad (1)$$

The main effect plot is shown in fig.4. It shows how the productivity varies when each of the factors in the model is changed from its low level to its high level, with all the factors held at the center of the experimental region.

The change in the rotation frequency of the lobes pump (X_1, min^{-1}) from low to high increase the productivity by 19,7 %. The larger internal diameter of the nozzle (X_2, mm) increase the productivity by 37,6 %. The increased rotation frequency of the working screw also favors the productivity by increasing it with 15,4 %.

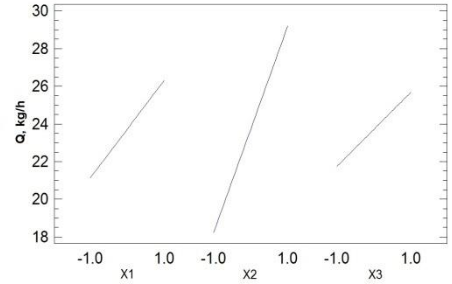

Fig.4 *Main effects plot*

The contours of equal output that show the impact of the rotation frequency of the lobes pump (X_1, min^{-1}) and the internal diameter of the nozzle (X_2, mm) over the productivity are presented on fig.5. It's obvious that the simultaneous increase in the values of both independent variables is increasing the productivity by 42,2 %. Increasing the rotation frequency of the lobes pump increases the amount of filling mass in the product and thus increase the productivity. The larger internal diameter increases the bright section between the nozzle and the needle. That leads to an increase in the density of the product, and reflects the productivity of the process. The increase of the rotation frequency of the lobes pump leads to an increase of the productivity by 11% when extruding with a nozzle X_2=9 mm, and by 18,6 % when using the nozzle with inner diameter X_2=10 mm.

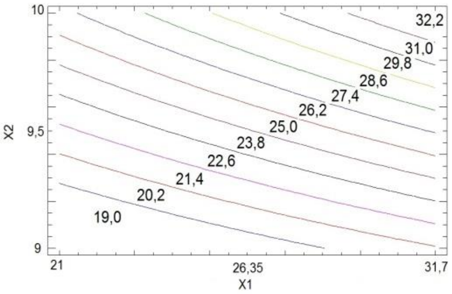

Fig.5 *Amendment of the productivity depending on the rotation frequency of the lobes pump (X_1, min^{-1}) and the inner diameter of the nozzle (X_2, mm)*

Expansion index

The expansion index is highest (EI=17,9) in lower levels of the three independent variables. Lowest average of the expansion index (EI=7,01) is obtained when all the independent variables are at their upper levels. The R-squared coefficient shows that in 99,69 % the change of the values of the independent variables will result in a change in the expansion index.

The Pareto chart (fig.6) shows, that the changes in the internal diameter of the nozzle (X_2,mm) and the rotation frequency of the lobes pump has the highest impact on the expansion index. The residual distribution diagram is presented on fig.7. It shows normal distribution of the residuals.

The following adequate regression model is obtained after processing the experimental results.

$$\mathbf{EI = 11,25 - 0,26X_1 – 3,78\,X_2 - 1,5X_3 + 0,23X_1X_2 – 1,06X_2X_3} \quad (2)$$

The main effects plot is presented at fig.8. It shows that the increase in the rotation frequency of the lobes pump x_1,min^{-1} reduces the expansion index by 4,6 %. The variation of the internal diameter of the nozzle from smaller to bigger, leads to an increase of the expansion index by 50,7 %. The low rotation frequency of the lobes pump brings a decrease of the expansion index by 23,4 %.

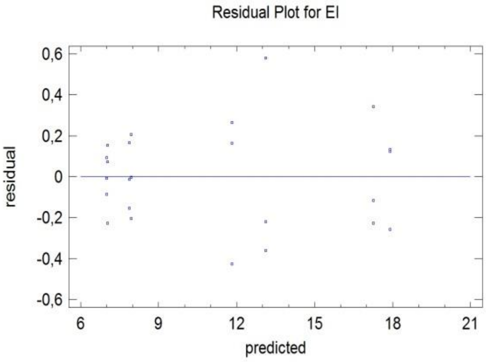

Fig.7 *Residual distribution diagram*

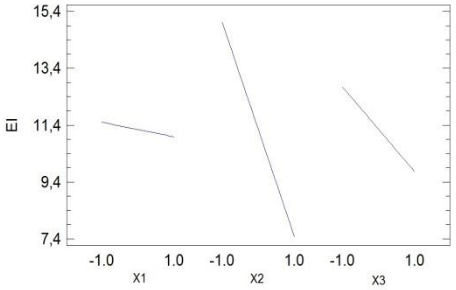

Fig.8 *Main effects plot for the expansion index*

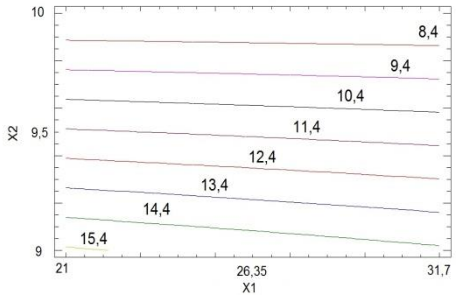

Fig.9 *Amendment of the expansion index, depending on the rotation frequency of the lobes pump (X_1,min^{-1}) and the internal diameter of the nozzle(X_2, mm)*

The joint impact of the rotation frequency of the lobes pump and the internal diameter of the nozzle is presented at fig.9. It's obvious that the joint increase of the two independent variables brings a decrease in the expansion index by 45,5%.

IV. Conclusions

A coextrusion die with submission of the filling mass perpendicular to the axis of the extruder is designed and constructed. It is suitable with the laboratory extruder "Brabender" 20 DN.

The authors obtained an adequate mathematical models describing the relation between the significant independent variables (rotation frequency of the lobes pump, inner diameter of the nozzle and rotation frequency of the extruder working screw) and the dependent variables : productivity and expansion index.

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THE MATERIALS BALANCE FOR THE MIGRATION PROCESS FROM THE ASSEMBLY METALLIC MATERIAL- LACQUERING SYSTEM OF THE PACKAGINGS IN THE CANNED FOOD STUFF (FOIS GRAS)

A. Buculei, M. P. Seritan

Faculty of Food Engeenering, University Stefan Cel Mare of Suceava, Romania

Abstract: *The interaction between the packagings and the food stuff consists in the substances transfer from the package into the foods and the other way around. There are also possible to occur chemical reactions in the package or reactions of the food stuff. These interactions can change the quality of the packed products but also the qualities of the package (the continous losss of its protection function). Thus, the main criteria for an optimal packing system is in most of the cases an minimal interaction. The led study was done for the determination of the heavy metals migration from the canned foods by realising a materials balance for the migration process from the assembly metallic material- lacquering system of the packagings in the canned food stuff (fois gras) . It was observed the fact that it was found in the foods a certain quantity of metals that during storage overpasses the admitted limit. There are some unavoidable processes of mass and substances exchange that are submitted to the second law of Fick that presents the time and space modification of ther concentration of migrating species. In some stages of the shelf life of the package such transfer processes can intensify leading even to the imposibility of food stuff further consumption.*

I. Introduction

The world level investigations of the last 30 years have prooved that the interaction between the contact materials with the food stuff apears as a predictible physical process [Doherty’2008, Banada’2011, Suhedan’2011,Vitrac’2007). The mass transfer is subdued to the Fick’s laws of difussion. Nvertheless the type of substances that appear during the interaction processes as well as the time during which they can appear need the leading of experimental measurements for to ensure the safety of the consumers. [Mohebbat’2011, Banada’2011].

The foods canned into a metallic can are almost always stable from the chemical point of view and have shelf lives between and five years. Besides the dry foods and certain stable foods from the microbiological and intrinsic point of view the canning of the other types foods is done by sterilization or pasteurization after their sealing in the package. Thus it is ensured their long term stability by eliminating the contaminations after the processing. [Krochta’2007]. The packaging materials safety is based on the ensurance that during the food stuff contact the unsafe chemical substances do not migrate from the material into the foods [Banada’2011].

The analitical determinations for the packaging materials are realized for::

1. To identify the package components;
2. To determine the nature of substances and their concentration (these substances can migrate into the packed foods and can have side effects upon the organoleptic properties such as the smell and the taste and the physico-chemical properties).

The stability of the system food product-package at the canning of the foods in metallic cans is influenced by several factors that target:

- the materials used for fabricating the metallic cans and caps;
- the materials used for the protection of the the metallic cans and caps;
- the characteristics of the canned foods;
- the foods conservation procsses in these types of cans;
- the interaction product- package by determining the components migration processes.

The researchers offer important information about the heavy metals migration helping to the increase of quality and canned foods safety in the metallic cans [Blunden’2003, Grassino’2010, Xia’2011].

II. Materials and methods

The studies and the experimental researches regarding the interaction between the food- metallic package were led on the fois gras cans. There were tested 213 cans with the dimensions of Ø 73 x 30 mm DS, with white inner lacquer PL1333-16, and PL 1014-59 grace outer lacquer.

For the experimental researches there were led analysis of the heavy metals from the canned products (fois gras), by atomic absorption spectrometry with graphite Shimadzu AA-6300 oven. This sudy followed the variation of the heavy metals migration from the package into the food during the storage time.

III. Results and discussion

In the case of the fois gras cans the initial reaction mass was considered to be formed by metals (led, cadmium, cooper, iron, zinc, tin) that enter in the structure of the assembly metal material- lacquering system of the can packagings and the sodium chloride solution from the food product fois gras.

The stoichiometric equation of the chemical process at the interaction surface between the food and metallic package in the case of the metal cans fois gras is the following:

$$Pb^0 + Cu^0 + Cd^0 + Zn^0 + Sn^0 + Fe^0 + 12Na^+Cl^- \\ \rightarrow PbCl_2 + CuCl_2 + CdCl_2 + ZnCl_2 + SnCl_2 + \\ + FeCl_2 + 12Na^+ \qquad (3.52)$$

Secondary reaction:

$$Na^+(OH)^- + R-COOH \rightarrow R-COO^-Na^+ + H_2O \qquad (3.53)$$

For to express the quantitative stage of the reaction of interaction between the food and metallic can at a certain moment we use the *dissolution degree* η_{A_k} *of a metallic contaminant or of an certain component* η_{A_i}. This measurement is defined as dissolution ***fraction of the metallic contaminant*** being expressed by the relation:

$$\eta_{Pb^0} = \frac{m^0_{Pb^0} - m_{Pb^0}}{m^0_{Pb^0}} = \frac{m^0_{Cu^0} - m_{Cu^0}}{\frac{M_{Cu^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cu^0}}{\nu_{Pb^0}} \cdot m^0_{Pb}} = \frac{m^0_{Cd^0} - m_{Cd^0}}{\frac{M_{Cd^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cd^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m^0_{Zn^0} - m_{Zn^0}}{\frac{M_{Zn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Zn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m^0_{Sn^0} - m_{Sn^0}}{\frac{M_{Sn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Sn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m^0_{Fe^0} - m_{Fe^0}}{\frac{M_{Fe^0}}{M_{Pb^0}} \cdot \frac{\nu_{Fe^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} =$$

$$= \frac{m^0_{HCl} - m_{HCl}}{\frac{M_{HCl}}{M_{Pb^0}} \cdot \frac{\nu_{HCl}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m_{PbCl_2} - m^0_{PbCl_2}}{\frac{M_{PbCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{PbCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m_{CuCl_2} - m^0_{CuCl_2}}{\frac{M_{CuCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{CuCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m_{FeCl_2} - m^0_{FeCl_2}}{\frac{M_{FeCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{FeCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} =$$

$$= \frac{m_{CdCl_2} - m^0_{CdCl_2}}{\frac{M_{CdCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{CdCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m_{ZnCl_2} - m^0_{ZnCl_2}}{\frac{M_{ZnCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{ZnCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m_{SnCl_2} - m^0_{SnCl_2}}{\frac{M_{SnCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{SnCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} = \frac{m_{H_2} - m^0_{H_2}}{\frac{M_{H_2}}{M_{Pb^0}} \cdot \frac{\nu_{H_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0}} \qquad (3.54)$$

The mass of each component in a certain moment is expressed by the following balance equations :

$$m_{Pb^0} = m^0_{Pb^0} - m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.55)$$

$$m_{Cu^0} = m^0_{Cu^0} - \frac{M_{Cu^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cu^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = m^0_{Cu^0} - \frac{M_{Cu^0}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.56)$$

$$m_{Cd^0} = m^0_{Cd^0} - \frac{M_{Cd^0}}{M_{Pb^0}} \cdot \frac{\nu_{Cd^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = m^0_{Cd^0} - \frac{M_{Cd^0}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.57)$$

$$m_{Zn^0} = m^0_{Zn^0} - \frac{M_{Zn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Zn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = m^0_{Zn^0} - \frac{M_{Zn^0}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.58)$$

$$m_{Sn^0} = m^0_{Sn^0} - \frac{M_{Sn^0}}{M_{Pb^0}} \cdot \frac{\nu_{Sn^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = m^0_{Sn^0} - \frac{M_{Sn^0}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.59)$$

$$m_{Fe^0} = m^0_{Fe^0} - \frac{M_{Fe^0}}{M_{Pb^0}} \cdot \frac{\nu_{Fe^0}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = m^0_{Fe^0} - \frac{M_{Fe^0}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.60)$$

$$m_{HCL} = m^0_{HCl} - \frac{M_{HCl}}{M_{Pb^0}} \cdot \frac{\nu_{HCl}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = m^0_{HCl} - 12 \cdot \frac{M_{HCl}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.61)$$

$$m_{PbCl_2} = \frac{M_{PbCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{PbCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = \frac{M_{PbCl_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.62)$$

$$m_{CuCl_2} = \frac{M_{CuCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{CuCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = \frac{M_{CuCl_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.63)$$

$$m_{CdCl_2} = \frac{M_{CdCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{CdCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = \frac{M_{CdCl_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.64)$$

$$m_{ZnCl_2} = \frac{M_{ZnCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{ZnCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = \frac{M_{ZnCl_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.65)$$

$$m_{SnCl_2} = \frac{M_{SnCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{SnCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = \frac{M_{SnCl_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.66)$$

$$m_{FeCl_2} = \frac{M_{FeCl_2}}{M_{Pb^0}} \cdot \frac{\nu_{FeCl_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = \frac{M_{FeCl_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.67)$$

$$m_{H_2} = \frac{M_{H_2}}{M_{Pb^0}} \cdot \frac{\nu_{H_2}}{\nu_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} = 6 \cdot \frac{M_{H_2}}{M_{Pb^0}} \cdot m^0_{Pb^0} \cdot \eta_{Pb^0} \qquad (3.68)$$

In the table 3.24 respectively 3.26. there are comparatively rendered the numerical values of the theoretical materials balance and respectively that of the real materials balance for the interaction surface processes between the food and metallic package in the case of the Pork meat in natural juice and Fois gras cans during their shelf life and the tables 3.25 and 3.27 present the calculations for the dissolution efficiency.

On the basis of the chemical equations and relations (3.38.), (3.39.) and (3.42.) there were obtained the numerical values for the theoretical and real materials balance for the interaction surface processes between the food and metallic package in the case of the Pork meat in natural juice and Fois gras cans during their shelf life being represented in the figures 3.45 respectively 3.46.

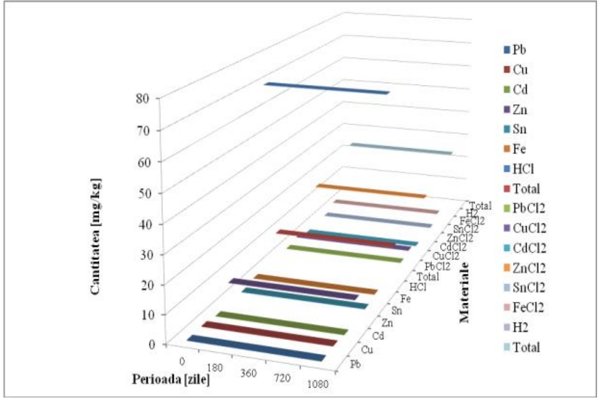

Fig. 3.45. *The materials balance of the migration process from the assembly metallic material- lacquering system of the packagings into the Fois gras food stuff*

IV. Conclusion

The increase of the food security requirements by the European Community legislation and more of the national legislation regarding the materials and objects that come in contact with the food or in the food simulants stuff targets both the maximum migration limits into the foods or in the food simulants for the materials constituents as well as the analysis methodology of those constituents.

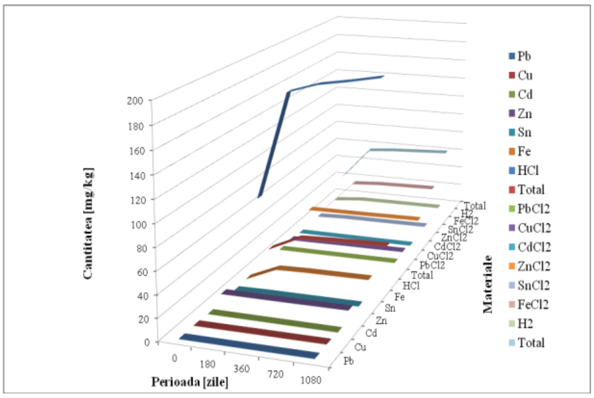

Fig. 3.46. *The materials balance of the migration process from the assembly metallic material- lacquering system of the packagings into the Pork in natural juice food stuff*

Taking on account the risks risen by the protection lacquers for the safety of the package there were necessary extensive tests for to establish the shelf life of the package suitable for the different types of canned foods. From the analysis of the exprimental data results the fact that after 24 and respectively 36 months of storage the heavy metals content of the products canned in metallic cans protected by white and yellow protection lacquers (with one and two inner layers of yellow lacquer) vary significantly.

As a conclusion for the led analysis it was prooved the fact that the constituents migration from the metallic can into the food takes place both ways no matter the package type is, the used cover layers are and even if the storage conditions are respected.

Tabel 3.26. *The materials balance of the migration process from the assembly metallic material- lacquering system of the packagings into the Fois gras food stuff*

Sample	Time [Days]	$Pb^0 + Cu^0 + Cd^0 + Zn^0 + Sn^0 + Fe^0 + 12Na^+Cl^- \rightarrow PbCl_2 + CuCl_2 + CdCl_2 + ZnCl_2 + SnCl_2 + FeCl_2 + 12Na^+$																
		The theoretical material balance																
		Entering materials								Leaving materials								
		Pb [mg/kg]	Cu [mg/kg]	Cd [mg/kg]	Zn [mg/kg]	Sn [mg/kg]	Fe [mg/kg]	HCl [mg/kg]	Total [mg/kg]	$PbCl_2$ [mg/kg]	$CuCl_2$ [mg/kg]	$CdCl_2$ [mg/kg]	$ZnCl_2$ [mg/kg]	$SnCl_2$ [mg/kg]	$FeCl_2$ [mg/kg]	$Cu(OH)_2$ [mg/kg]	H_2 [mg/kg]	Total [mg/kg]
Fois gras	0	1,09	6,95	0,04	6,67	0,05	135	1150,368	149,8	1,46386473	14,660156	0,06535714	13,845303	0,07983193	306,160714	31,51694	336,275227	1,09
	180	1,09	6,95	0,04	6,67	0,05	135	1150,368	149,8	1,46386473	14,660156	0,06535714	13,845303	0,07983193	306,160714	32,51694	336,275227	1,09
	360	1,09	6,95	0,04	6,67	0,05	135	1150,368	149,8	1,46386473	14,660156	0,06535714	13,845303	0,07983193	306,160714	33,51694	336,275227	1,09
	720	1,09	6,95	0,04	6,67	0,05	135	1150,368	149,8	1,46386473	14,660156	0,06535714	13,845303	0,07983193	306,160714	34,51694	336,275227	1,09
	1080	1,09	6,95	0,04	6,67	0,05	135	1150,368	149,8	1,46386473	14,660156	0,06535714	13,845303	0,07983193	306,160714	35,51694	336,275227	1,09
Sample	Time [Days]	**The real material balance**																
		Entering materials								Leaving materials								
		Pb [mg/kg]	Cu [mg/kg]	Cd [mg/kg]	Zn [mg/kg]	Sn [mg/kg]	Fe [mg/kg]	HCl [mg/kg]	Total [mg/kg]	$PbCl_2$ [mg/kg]	$CuCl_2$ [mg/kg]	$CdCl_2$ [mg/kg]	$ZnCl_2$ [mg/kg]	$SnCl_2$ [mg/kg]	$FeCl_2$ [mg/kg]	$Cu(OH)_2$ [mg/kg]	H_2 [mg/kg]	Total [mg/kg]
Fois gras	0	1,09	6,95	0,04	6,67	0,05	135	1150,368	149,8	1,46386473	14,660156	0,06535714	13,845303	0,07983193	306,160714	31,51694	336,275227	1,09
	180	1,11	7,04	0,04	6,67	0,06	147,8	1251,177653	162,72	1,49072464	14,85	0,06535714	13,845303	0,09579832	335,189286	34,2788398	365,536469	1,11
	360	1,16	7,12	0,04	6,7	0,1	154,12	1301,608696	169,24	1,5578744	15,01875	0,06535714	13,9075758	0,15966387	349,522143	35,66051223	380,231364	1,16
	720	1,21	7,21	0,04	6,8	0,15	168,45	1414,643235	183,77	1,62502415	15,208594	0,06535714	14,1151515	0,2394958	382,020536	38,7742239	413,274158	1,21
	1080	1,32	7,3	0,04	6,89	0,2	172,12	1445,593813	187,87	1,77275362	15,398438	0,06535714	14,3019697	0,31932773	390,343571	39,60530994	422,201417	1,32

Tabel 3.27. *The dissolution efficiency*

Sample	Time [Days]	**The dissolution efficiency**						
		$PbCl_2$	$CuCl_2$	$CdCl_2$	$ZnCl_2$	$SnCl_2$	$FeCl_2$	Total
Rehydrated canned peas	0	1	1	1	1	1	1	1
	180	1,01834863	1,01294966	1	1	1,20000005	1,09481482	1,08701575
	360	1,06422019	1,02446045	1	1,00449776	2,00000013	1,14162963	1,13071476
	720	1,11009174	1,03741011	1	1,01949026	3,00000013	1,24777778	1,22897592
	1080	1,21100918	1,05035976	1	1,03298351	4,00000013	1,27496296	1,2555234

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MODEL STUDIES OF THE HYDRODYNAMICS OF FLOW IN CORRUGATED TUBES

M. S. Angelov, P. R. Raynov

University of Food Technologies,
26, Maritza Blvd., 4002 Plovdiv, Bulgaria

Abstract: *This paper presents model studies of flow in corrugated tubes. For the mathematical description of the flow the equation of motion for the three-dimensional case, written as to the average at the time variables, is used. To close the system of differential equations of movement a k-ω model of turbulence is used. Dependences for the influence of the Reynolds number and the geometrical parameter* ***p/e*** *on the velocity field and turbulent kinetic energy were obtained. For the purpose of the work a three-dimensional physical model with geometry corresponding to the real existing model is designed. A computing mesh corresponding for the model was created, as well as study of the solution's independence by the density and the shape of the mesh was done. The applicability is aimed at optimizing heat exchangers with fixed sizes and positions, and tubes for solar collectors.*

Key words: CFD, modeling, intensification, hydrodynamics.

I. Introduction

Methods for increasing the turbulence of the flow can be divided into two main groups: passive-methods (do not require the direct use of an external energy source), active (do require the direct use of an external energy source) and also there is a combined method (when above mentioned methods are used together) [3].

Basic passive techniques may include: surface treatment, pre-wall turbolizer ("roughness"), "developed" areas, devices for mixing of a flow, devices for rotating of a flow, devices affecting the surface tension, additives for fluids.

Basic active techniques may include: mechanical additives, surface vibration, vibration of the flow, electrostatic, suction and blowing in the area of the boundary layer, impact through jet streams.

From the combined (joint) intensification the greatest application have found: pre-wall turbolizer with helix bands, pre-wall turbolizer with acoustic vibration of the flow, internally finned tubes with twisted tapes, externally finned tubes in a fluidized bed, externally finned tubes subjected to vibration low-finned ("rough" channels) with longitudinal vortex generators.

The intensification of a turbulent mixing can be achieved through the use of some of these methods. As a result of the intensification a thinning of the boundary layer is observed, which is accompanied with detachment of the flow and its sticking back to the wall. The change in geometry of the flow leads to change into the flow structure. A circulating flow is being appeared and that leads to further intensification of the turbulent exchange.

II. Materials and methods

The aim of this work was to perform a model study of the hydrodynamics of the flow in corrugated tubes. The applicability is aimed at optimizing heat exchangers with fixed sizes and positions, and tubes for solar collectors. For the mathematical description of the flow the equation of motion for the three-dimensional case, written as to the average at the time variables, is used:

$$\rho\frac{d\bar{u}}{dt} = \rho X - \frac{\partial\bar{p}}{\partial x} + \mu\Delta\bar{u} - \rho\left(\frac{\partial\overline{u'^2}}{\partial x} + \frac{\partial\overline{u'v'}}{\partial y} + \frac{\partial\overline{u'w'}}{\partial z}\right) \quad (1)$$

$$\rho\frac{d\bar{v}}{dt} = \rho Y - \frac{\partial\bar{p}}{\partial y} + \mu\Delta\bar{v} - \rho\left(\frac{\partial\overline{u'v'}}{\partial x} + \frac{\partial\overline{v'^2}}{\partial y} + \frac{\partial\overline{v'w'}}{\partial z}\right) \quad (2)$$

$$\rho\frac{d\bar{w}}{dt} = \rho Z - \frac{\partial p}{\partial z} + \mu\Delta\bar{w} - \rho\left(\frac{\partial\overline{u'w'}}{\partial x} + \frac{\partial\overline{v'w'}}{\partial y} + \frac{\partial\overline{w'^2}}{\partial z}\right) \quad (3)$$

The system of equations is supplemented with equations that describe one of the models of turbulence known as k-ω turbulence model [5]. This model was chosen by a comparative analysis of models of turbulence which are being used for solving of flows with separation and turbulence near the streamlined surfaces.

Turbulent kinetic energy (k) and the specific dissipation rate (ω) are obtained from the following transport equations:

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_i}(\rho k u_i) = \frac{\partial}{\partial x_j}\left(\Gamma_k\frac{\partial k}{\partial x_j}\right) + G_k - Y_k + S_k \quad (4)$$

$$\frac{\partial}{\partial t}(\rho\omega) + \frac{\partial}{\partial x_i}(\rho\omega u_i) = \frac{\partial}{\partial x_j}\left(\Gamma_\omega\frac{\partial\omega}{\partial x_j}\right) + G_\omega - Y_\omega + S_\omega \quad (5)$$

In these equations, G_k represents the generation of turbulence kinetic energy due to mean velocity gradients. G_ω represents the generation of ω. Γ_k and Γ_ω represent the effective diffusivity of k and ω, respectively. Y_k and Y_ω represent the dissipation of k and ω due to turbulence. All of the above terms are calculated as described below. S_k and S_ω are user-defined source terms. The effective diffusivities for the k-ω model are given by:

$$\Gamma_k = \mu + \frac{\mu_t}{\sigma_k} \tag{6}$$

$$\Gamma_\omega = \mu + \frac{\mu_t}{\sigma_\omega} \tag{7}$$

where: σ_k and σ_ω are the turbulent Prandtl numbers for k and ω, respectively. The turbulent viscosity, μ_t, is computed by combining k and ω as follows:

$$\mu_t = a^* \frac{\rho.k}{\omega} \tag{8}$$

The coefficient a^* damps the turbulent viscosity causing a low-Reynolds number correction. It is given by:

$$a^* = a_\omega^*.\left(\frac{a_0^* + Re_t/R_k}{1 + Re_t/R_k}\right) \tag{9}$$

where:

$$Re_t = \frac{\rho.k}{\mu.\omega},\ R_k = 6,\ a_0^* = \frac{\beta_t}{3},\ \beta_i = 0.072 \tag{10}$$

In the high-Reynolds number form of the k-ω model, $a^* = a_\infty^* = 1$.

The term G_k represents the production of turbulence kinetic energy. From the exact equation for the transport of k, this term may be defined as:

$$G_k = -\rho\overline{u_i' u_j'}\frac{\partial u_j}{\partial x_i} \tag{11}$$

To evaluate G_k in a manner consistent with the Boussinesq hypothesis,

$$G_k = \mu_t S^2, \tag{12}$$

where: S is the modulus of the mean rate-of-strain tensor, defined in the same way as for the k-ε model.

The production of ω is given by:

$$G_\omega = a\frac{\omega}{k}G_k, \tag{13}$$

where: G_k is given by Equation (11). The coefficient a is given by:

$$a = \frac{a_\infty}{a^*}\left(\frac{a_0 + Re_t/R_\omega}{1 + Re_t/R_\omega}\right), \tag{14}$$

where: $R_\omega = 2{,}95$, a^* and Re_t are given by Equation (9) and Equation (10), respectively.

The dissipation of k is given by:

$$Y_k = \rho\beta^* f_{\beta^*} k\omega \tag{15}$$

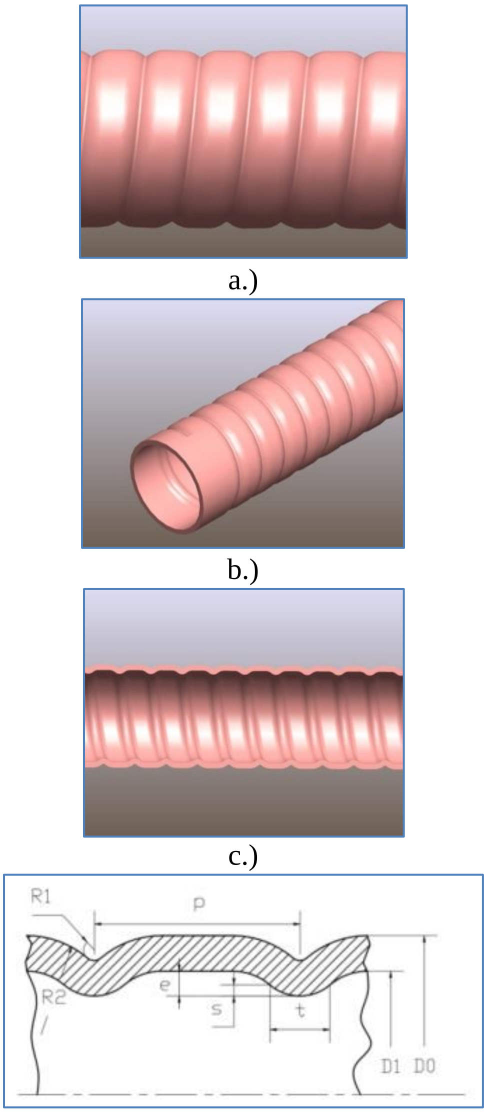
where f_{β^*} and β^* are given by [5].

The dissipation of ω is given by:

$$Y_\omega = \rho\beta f_\beta \omega^2 \tag{16}$$

where β, f_β and model constants given by [5].

Schematic of the physical model test tube is shown in Fig.1 a.), b.), c.) and d.) showing the geometric parameters that define the shape and size of the turbolizer. The step between turns is denoted by **p**, and the depth with **e**.



a.)

b.)

c.)

d.)

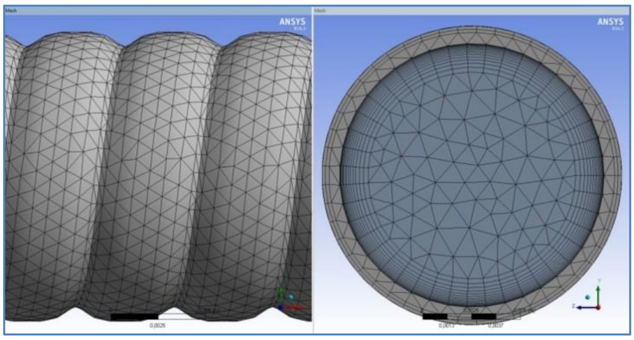
Fig.1. *Physical model of the corrugated tube.*

The three-dimensional physical model is designed by the software SolidWorks. The specificities when creating a model are mainly related with the assignment of geometrical parameters of the threads, their step, depth and angle of the helix (Fig. 1 and Tab. 1.1). Tab. 1.1 shows the basic geometry of the two tubes examined by us [7]:

Table 1. *Geometric parameters of the studied tubes.*

№	D1 mm	D0 mm	p mm	e mm	t mm	s mm	β mm	p/e
5030	13,51	15,31	5,19	0,767	1,836	0,371	83	6,77
5060	14	15,65	4,78	0,578	1,392	0,257	83,8	8,27

The influence of the individual parameters change on the flow is studied by the software ANSYS FLUENT. The design of the computational grid through discretization of the computational area is the next important step in the study. By the fact that transmission processes are carried out in the zone near the wall a corresponding mesh is created with the required density (4,434,340 elements and 1,702,250 nodes in a maximum absolute cell size 0.001 m). In addition, 15 layers near the wall also were created, in this way the boundary layer zone is being discretized by the mesh fig.2. a.), b.) and fig.3.



a.) *general view* b.) *distribution in the cross section*

Fig.2. *General view of the mesh created to make the calculation.*

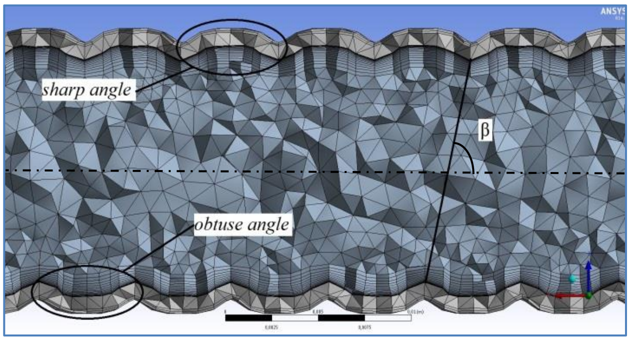


Fig.3. *General view of the mesh along the flow near the wall and in the mainstream.*

The independence of the decision by the density of the mesh was studied. For that purpose three different mesh densities are being compared. The verification of the results is made by comparison with experimental results in relation to the friction coefficient [3, 7]. The mechanical energy loss, due to axial flow, tangential flow and vortex mixing could be combined in one equation [6]:

$$f = \frac{\Delta P_{tot}.D_{\text{Н}}}{2.\rho.L.u_m^2} = \frac{(\Delta P_a+\Delta P_t+\Delta P_V).D_{\text{Н}}}{2.\rho.L.u_m^2}\ , \qquad (17)$$

when: $f = f_a + f_t + f_V = f(Re_{\text{Н}})$. (18)

After the density is being established all the regimes of simulations are carried out.

III. Analysis of results and discussion

Studying the character of the flow in the pipe with the shown geometry indicates the presence of a mainstream. That mainstream is being influenced by the **p/e** ratio and by the angle of the helix β. The boundary layer is being influenced also by the p/e ratio.

The character of the flow in a pipe with turbolizers of this type is expected to depend on the Reynolds number, the ratio **p/e** and the inclination angle of the helical channel. The flow detaches from the top of the turbolizer and sticks again at some distance alongside to the flow. The flow expressed one character at **p/e > 9** and another character within **7 < p/e < 9**.

On Fig.4. a.), b.) and c.) are shown the velocity vectors for **p/e = 6,77** at three different numbers of Reynolds at sharp angle of the helix shown in Fig. 3.

On Fig.5. a.), b.) and c.) are shown the velocity vectors for **p/e = 6,77** at three different numbers of Reynolds at obtuse angle of the helix.

The analysis of the velocity field shows a significant difference in the velocity distribution near the streamlined wall of the sharp and of the obtuse angle area of the helix. Typically for the velocity field is the presence of a flow detachment and formation of a circulating zone near the wall. This is an indication of the boundary layer turbolizing. Increasing of the number of Reynolds leads to a decrease of the circulating area and to a decrease of the distance of re-sticking of the flow to the wall. The tendency of the flow detachment and the formation of circulating area are being kept at obtuse angle helical channel. The difference is that the point of the flow detachment is being found at the immediate vicinity of the curvature of the ribbed wall. The sticking point of the flow is at the beginning of the next round of the helix, as the distance to the place of sticking decreases with increasing the number of Reynolds. We may say that the entire area of the threads in this zone is filled with a circulating flow.

On Fig.6. a.), b.) and c.) are shown the velocity vectors for **p/e = 8,27** at three different numbers of Reynolds at sharp angle of the helix.

Flow detachment and its sticking again to the wall characterizes the flow and also the presence of the circulating area. The size of the circulation area decreased with increasing of the Reynolds number.

On Fig.7. a.), b.) and c.) are shown the velocity vectors for **p/e = 8,27** at three different numbers of Reynolds at obtuse angle of the helix.

The size of the circulation area decreased significantly with increasing of the Reynolds number. Compared with the area at sharp angle of the helix the alteration is greater. Sticking of the flow back to the wall is much faster and reaches the wall earlier. Flow has expressed a different character at **p/e > 9** compared with **p/e < 9**.

Turbulent kinetic energy is a measure of turbolizing of the flow as a result of the presence of a helix in the streamlined wall. Research on the influence of the Reynolds number and of the **p/e** ratio on the kinetic energy change was made.

On Fig.8. a.), b.) and c.) are shown the turbulent kinetic energy for **p/e = 6,77** at three different numbers of Reynolds at sharp angle of the helix.

On Fig.9. a.), b.) and c.) are shown the turbulent kinetic energy for **p/e = 6,77** at three different numbers of Reynolds at obtuse angle of the helix.

On Fig.10. a.), b.) and c.) are shown the turbulent kinetic energy for **p/e = 8,27** at three different numbers of Reynolds at sharp angle of the helix.

On Fig.11. a.), b.) and c.) are shown the turbulent kinetic energy for **p/e = 8,27** at three different numbers of Reynolds at obtuse angle of the helix.

Turbulent kinetic energy is one of the most important parameters that alter the structure of the boundary layer. It is a measure of the turbulent intensity. From the results shown in Fig. 8 to11 we can conclude that the magnitude of the turbulent kinetic energy gradient increases after the area of the thread and subsequently sharply decrease in the area of the flow sticking. We can trace the location of the kinetic energy maximum at different Reynolds numbers and different values of the geometrical parameter **p/e**.

With increasing of the Reynolds number, the location of the turbulent kinetic energy maximum approaches the wall. That same trend remains with increasing of the geometric parameter **p/e**.

IV. Conclusion

The analysis of the main hydrodynamic dependencies showed**:**

1. The presence of turbolizers from the studied type leads to appearance of flow detachment and appearance of a recirculating flow near the wall.
2. The value of the geometric parameter of turbolizer (**p/e**) strongly influences the generation of a recirculating flow.
3. The character of the flow near the wall differs from the flow symmetry axis. That difference leads to appearance of a tangential velocity, which increases the mixing (turbolizing).
4. The resultant velocity vector causes a vortex flow perpendicular to the main stream. The vortex flow continuously destroys (mixes) the boundary layer along the wall.

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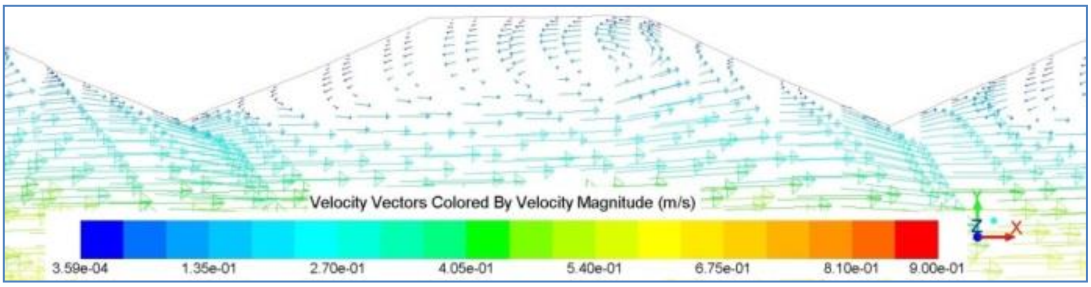
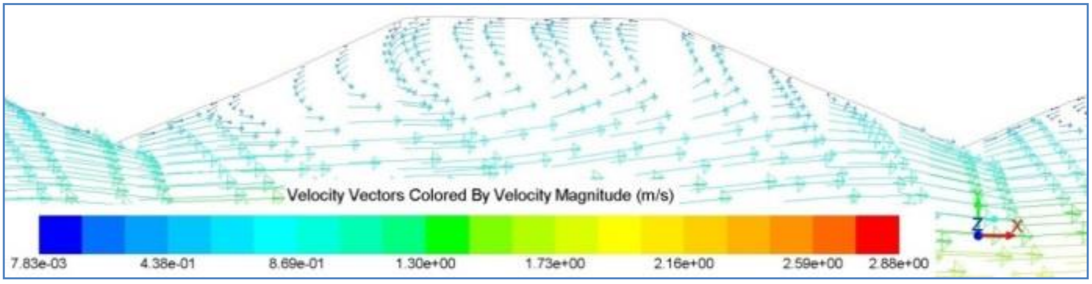
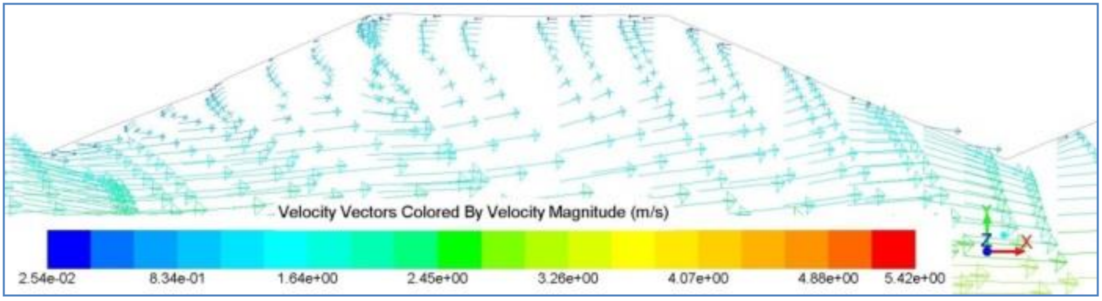
Attachment 1



a.) *Re_1=6141*

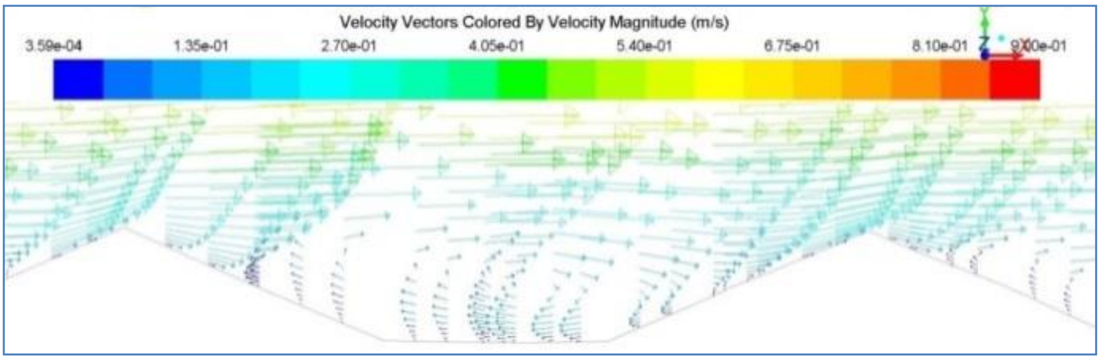


b.) *Re_2=19651*



c.) *Re_3=36845*

Fig.4. *Distribution of velocity vectors at three different numbers of Reynolds at sharp angle of the helix.*



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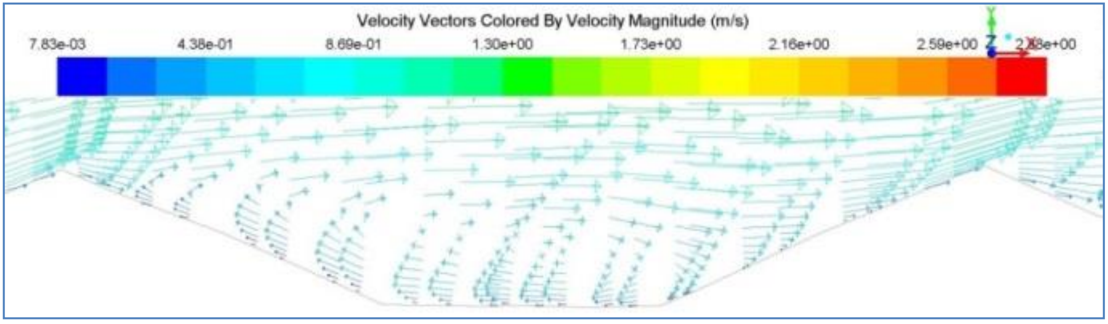
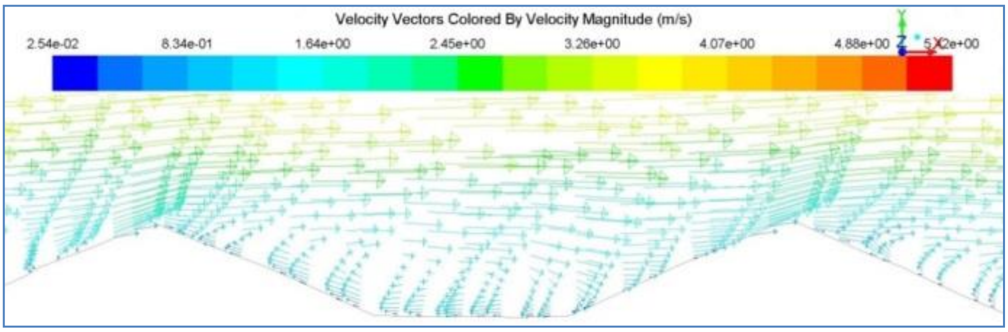
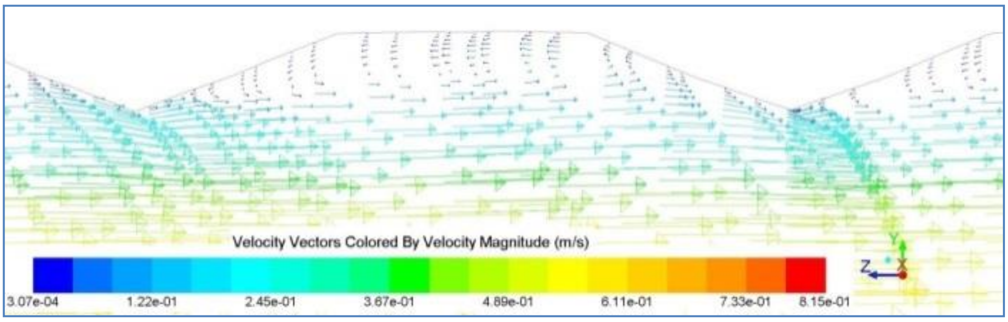


b.) *Re_2=19651*

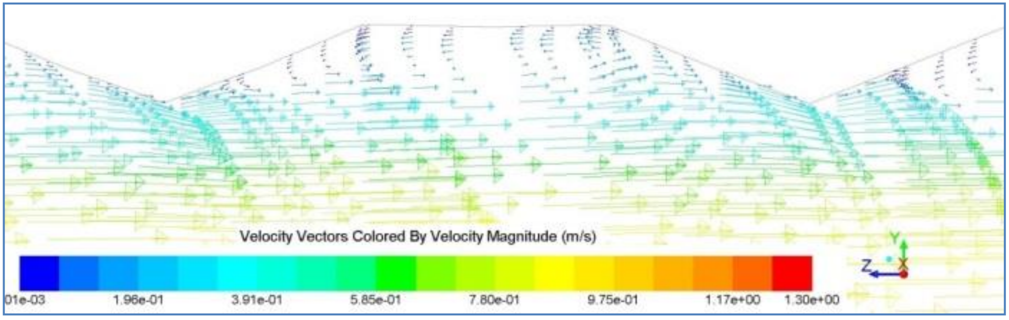


c.) Re_3=36845

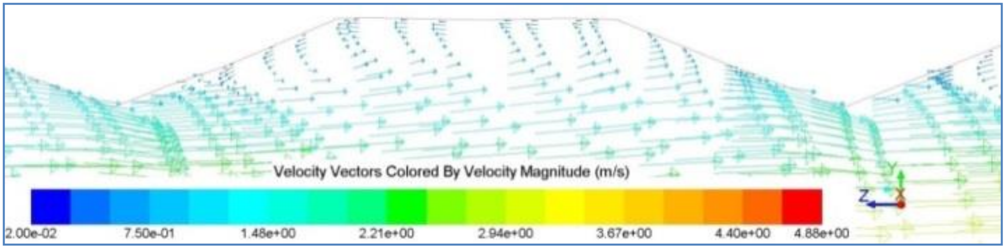
Fig.5. *Distribution of velocity vectors at three different numbers of Reynolds at obtuse angle of the helix.*



a.) Re_1=6363

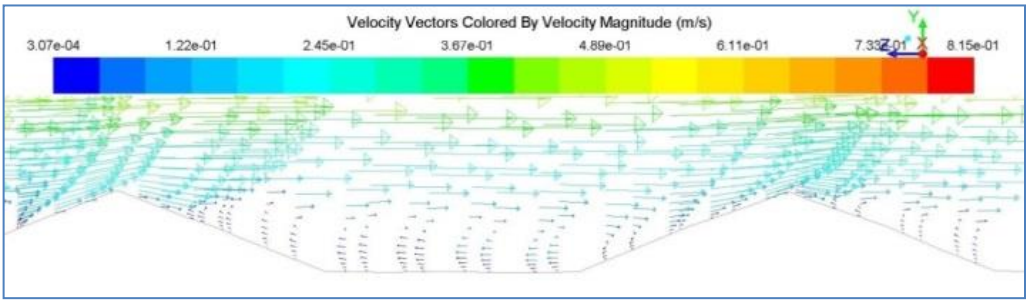


b.) Re_2=20362

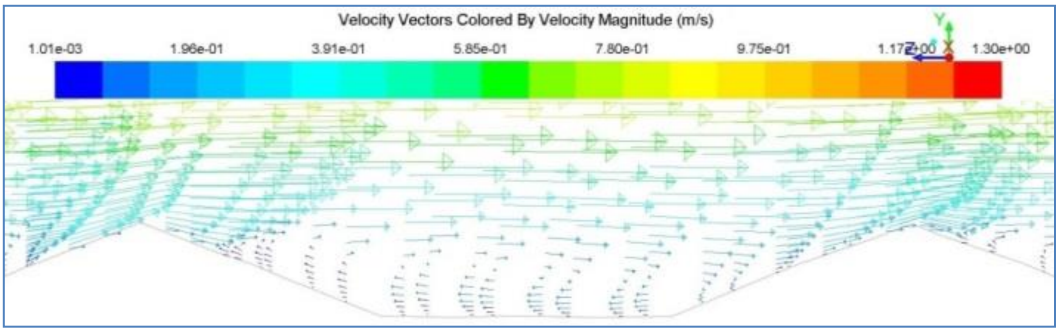


c.) Re_3=38178

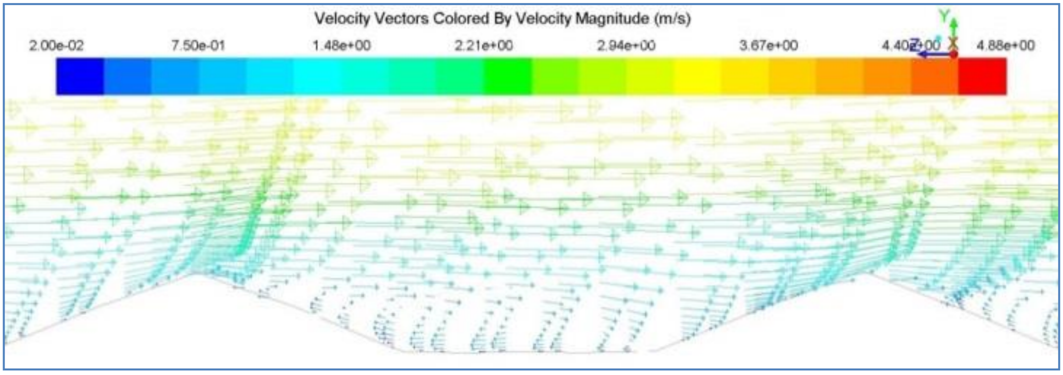
Fig.6 *Distribution of velocity vectors at three different numbers of Reynolds at sharp angle of the helix.*



a.) Re_1=6363

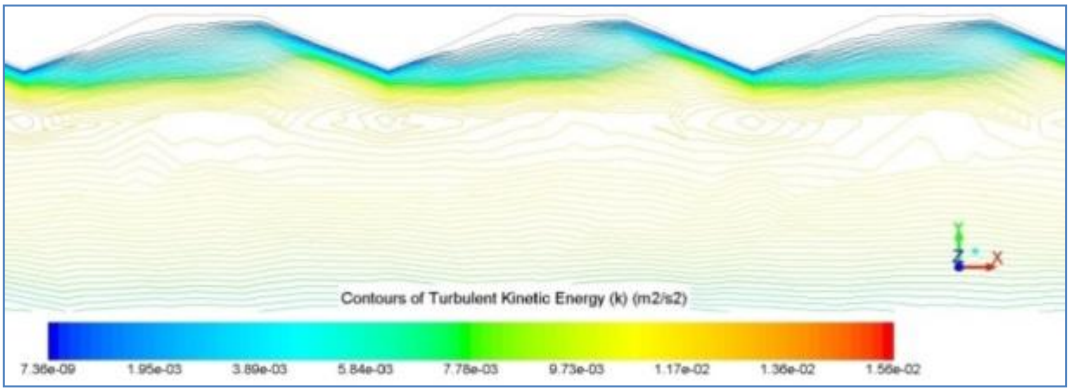


b.) Re_2=20362



c.) Re_3=38178

Fig.7. *Distribution of velocity vectors at three different numbers of Reynolds at obtuse angle of the helix.*



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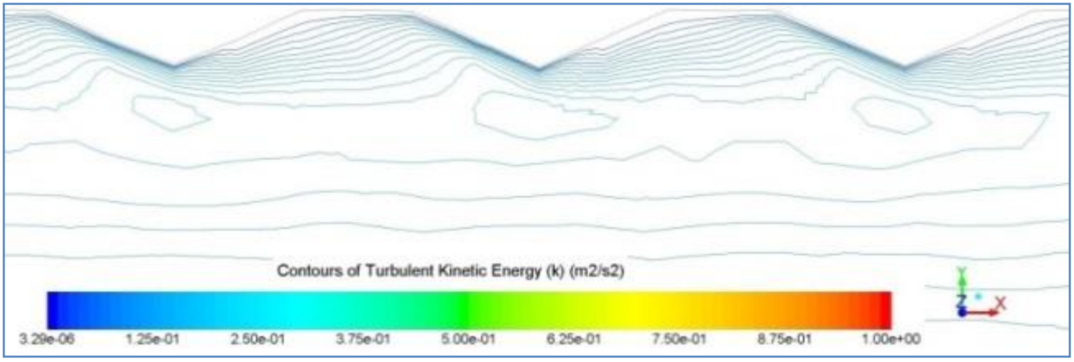
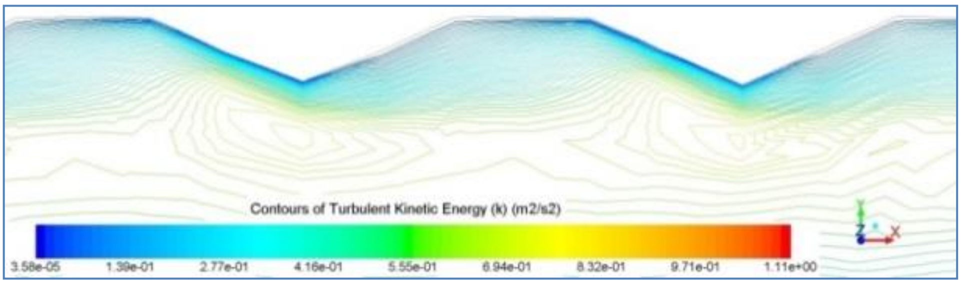
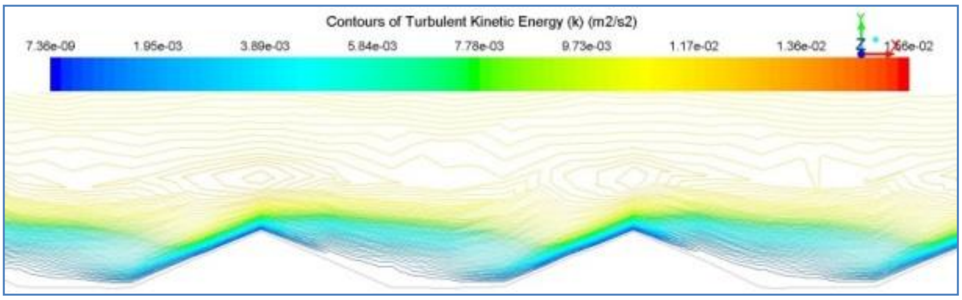


b.) Re_2=19651

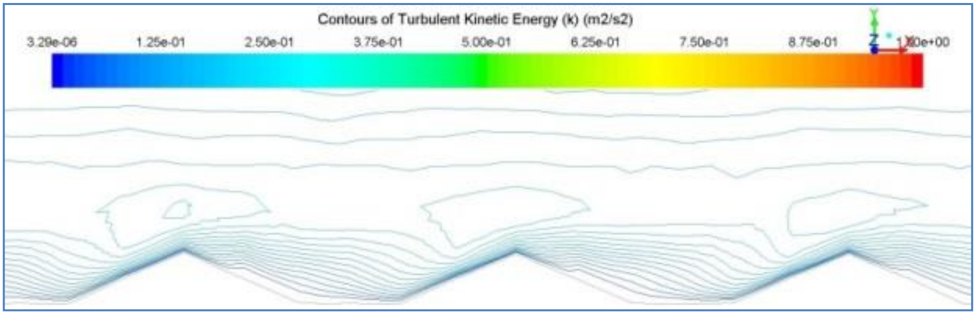


c.) *Re$_3$=36845*

Fig.8. *The change in kinetic energy at three different numbers of Reynolds at sharp angle of the helix.*



a.) *Re$_1$=6141*



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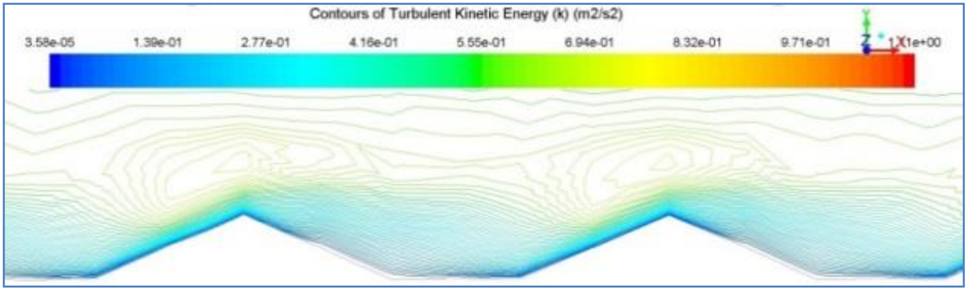
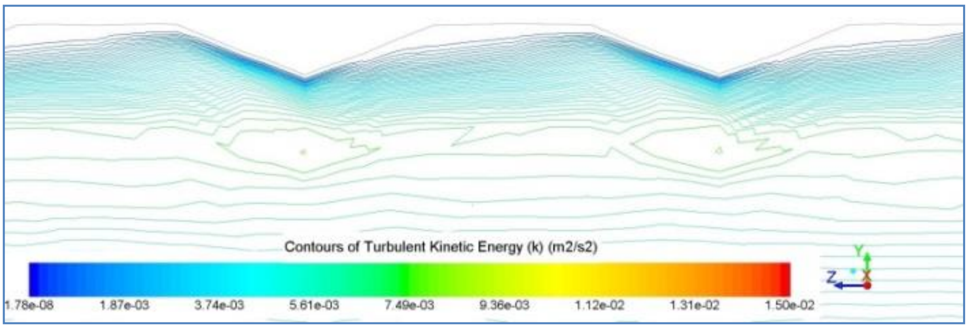
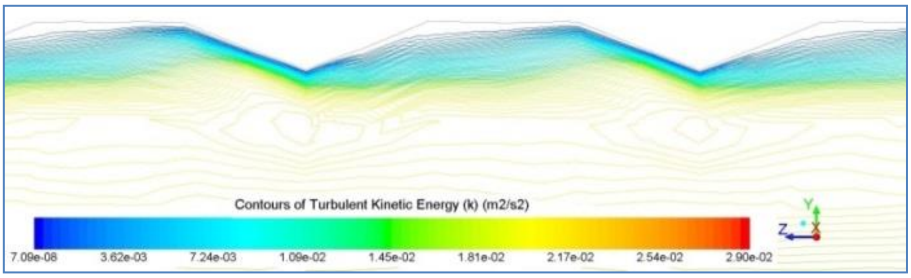


c.) *Re$_3$=36845*

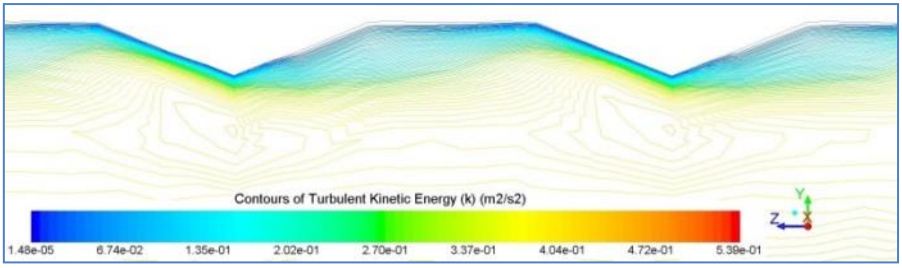
Fig.9. *The change in kinetic energy at three different numbers of Reynolds at obtuse angle of the helix.*



a.) *Re$_1$=6363*

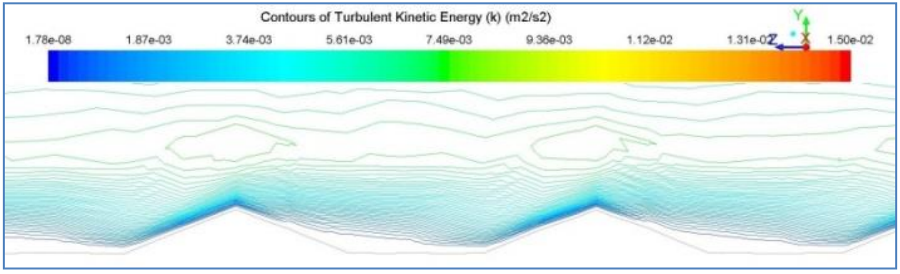


b.) *Re*$_2$*=20362*

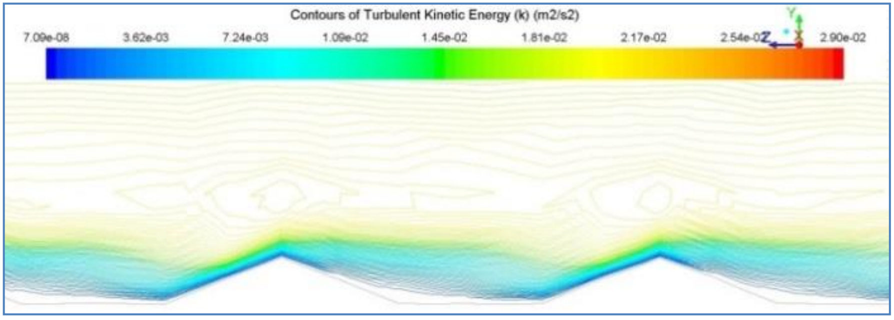


c.) *Re*$_3$*=38178*

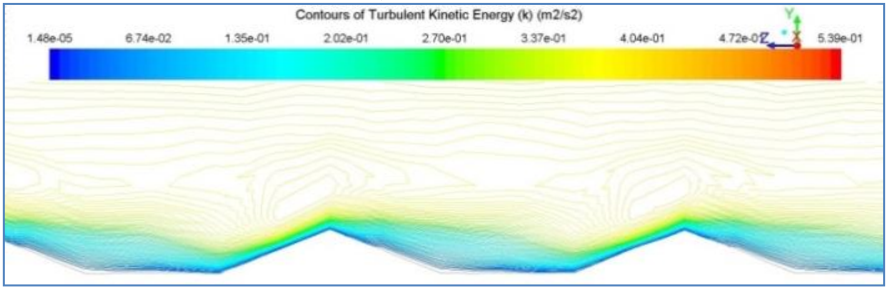
Fig.10 *The change in kinetic energy at three different numbers of Reynolds at sharp angle of the helix.*



a.) *Re*$_1$*=6363*



b.) *Re*$_2$*=20362*



c.) *Re*$_3$*=38178*

Fig.11. *The change in kinetic energy at three different numbers of Reynolds at obtuse angle of the helix.*

NUMERICAL ANALYSIS OF TWO-PHASE NON-ISOTHERMAL NANO JETS

M. S. Angelov[1], I. S. Antonov[2], D. P. Stoeva[1], P.R.Rainov[1], S. Pleshkova-Bekiarska[2]

[1]University of Food Technologies 26, Maritza Blvd., 4002 Plovdiv
[2]Technical University of Sofia

Abstract: *The choice of suitable mathematical model and corresponding model of turbulent shear stresses is a very important issue while analyzing turbulent two-phase nano jets. We accept two-fluid scheme of the jet, according to which in every point of the area and in every moment, both phases have different densities, velocities and temperatures. The relation between phases in the equations for movement and heat transfer are the powers of phase interaction, which are accepted to be essential for the corresponding jet. For closing the equation system for movement, we apply one modification of the* $\kappa-\varepsilon$ *model of turbulence. It uses two equations for the turbulent kinetic energy for the phases and one for the dissipation of turbulent kinetic energy of the carrier phase* $\kappa_g-\kappa_p-\varepsilon$ *model.*

Keywords: turbulent two-phase nano jets, $\kappa_g-\kappa_p-\varepsilon$ model, numerical analysis

I. Introduction

The two-phase character of the jet influences the fixation of equations for turbulent energy and dissipation of turbulent energy by adding additional dissipative terms. One of the accurate methods for describing heterogeneous dispersed two-phase environments is based on the concept of multi velocity interpenetrating continuum. We take for granted the existence of various fields of the velocities, temperatures and densities of the phases - a carrier phase and a phase of the admixtures. The phases have their own velocity, density and temperature in every point of the jet. The object of the research is numerical modeling of two-phase non-isothermal turbulent nano jet, which flows into still environment from the carrier phase with different temperature, compared to the temperature of the nano-jet.

Many modern technologies and apparatus require the dispersion of tiny quantities of fluids. Such necessity appears when there is a requirement for very fast evaporation of cryogenic fluids in special equipment for generating aerosols or mist in a particular space in order to increase the moisture content of the air (in fire-fighting devices, air handling units, when spreading liquid medicines), by obtaining pure substances in laboratory conditions.

For achieving of very thin dispersion at the level of nanoparts or micrometers ($d_p \leq 10 \div 20\mu m$), a very small flow rate is used – about Q=5÷10 *l*/h and the dimension of the nozzle unit, from which the jet comes, is recommended to be about $d_д \approx 0{,}25 \div 5mm$. The use of ultrasonic emitter, piezoelectric effect and others are recommended for use when thing dispersion is required. For example, if we have dispersed liquid drops with radius $d_p=10\mu m$, if we use electrical charge E=300V, the drops are destroyed under the power of the aerodynamic forces and the radius of the newly formed drops [1] is five times smaller $r = 2.10^{-6}$m. If we increase the charge to E=350V the radius decreases to $r = 892.10^{-9}$ m and at E=400V then $r = 0{,}4.10^{-6}$m (400.10^{-9} m). We can conclude by this method of dispersion that by increasing the electrical charge we can successfully decrease the dimension of the finely dispersed drops.

In many cases it is of particular importance to leaving the finely dispersed liquid droplets in a state of hovering. It is known that this condition occurs when the force of its own weight $\overrightarrow{f_g}$ is balanced or is lower than the aerodynamic resistance of the free falling of the droplet or the particle $\overrightarrow{f_R}$,as:

$$\overrightarrow{f_g} = \vec{g}.m_p \tag{1}$$

$$\overrightarrow{f_R} = C_R.S.\rho_g \frac{V_{cn}^2}{2} \tag{2}$$

where: m_p - the mass of the particle $m_p=\rho_p.W$ - density of the particle volume; C_R - aerodynamic resistance coefficient; S - area of the middle section of the droplet, ρ_p and ρ_g - density of the admixtures and the gas air environment; V_{cn} - free falling, resp. $V_{cn}=V_V$; V - velocity of hovering. Equalizing both forces in (1) and (2) the result is the of hovering, if it is considered lower than the velocity of free falling ($V_V < V_{cn}$) will be

$$V_V \leq \sqrt{\frac{2gm_p}{C_R S \rho_g}} \tag{3}$$

As the Reynolds number of admixtures $Re_p = \frac{V_r.d_p}{\nu}$ (when $V_r = V_g - V_p$, d_p-diameter of the admixture particle viscosity of the gas environment) is always lower than one at level of nano particles ($Re_p < 1$), then the coefficient C_R is calculated by the Stoke's law:

The essential question, arising from the movement of droplets of nano-parts level is: Where is point in which the hovering velosity will be reached? This means at what level x from the outgoing nozzle the velocity of the nano-particle will reach V_V. In order to achieve the necessary information, the flow must be studied as a movement of two-phase mixture, on which the two-phase model is applied, as described in [2] and [3].

I. Basic equations for movement

The two-phase axial-symmetric non-isothermal non-jet is described in Decartes coordinate system of equations:

$$C_R = \frac{24}{Re_p} \tag{4}$$

$$\partial / \partial x \left[y^j U_g \rho_g \right] + \partial / \partial y \left[y^j V_g \rho_g \right] = 0 \tag{5}$$

$$\partial / \partial x \left[y^j U_p \rho_p \right] + \partial / \partial y \left[y^j V_p \rho_p \right] = 0 \tag{6}$$

$$\left[y^j U_p \right] \partial \rho_p / \partial x + \left[y^j V_p \right] \partial \rho_p / \partial y = -\partial / \partial y \left[y^j \overline{\rho'_p V'_p} \right] - \overline{\rho'_p V'_p} \tag{7}$$

$$\left[y^j \rho_g U_g \right] \partial U_g / \partial x + \left[y^j \rho_g V_g \right] \partial U_g / \partial y = -\partial / \partial y \left[y^j \rho_g \overline{U'_g V'_g} \right] - F_x y^j \tag{8}$$

$$\begin{gathered} \left[y^j \rho_p u_p \right] \partial u_p / \partial x + \left[y^j (\rho_p V_p + \overline{\rho'_p V'_p}) \right] \partial U_p / \partial y = \\ = -\partial / \partial y \left[y^j \rho_p \overline{U'_p V'_p} \right] + F_x y^j \end{gathered} \tag{9}$$

$$\begin{gathered} \left[y^j \rho_p U_p \right] \partial h_p / \partial x + \left[y^j (\rho_p V_p + \overline{\rho'_g V'_g}) \right] \partial h_p / \partial x = \\ = -\partial / \partial y \left[y^j \rho_p \overline{h'_p V'_p} \right] + Q y^j \end{gathered} \tag{10}$$

$$\begin{gathered} \left[y^j \rho_g U_g \right] \partial h_g / \partial x + \left[y^j \rho_g V_g \right] \partial h_g / \partial x = -\partial / \partial y \left[y^j \rho_g \overline{h'_g V'_g} \right] - \\ - \left[y^j \rho_g \overline{h'_g V'_g} \right] \partial U_g / \partial y - Q y^j + F_x y^j \left(U_g - U_p \right) + F_y y^j \left(V_g - V_p \right) - \\ - \sum_{i=1}^{3} \overline{F'_i V'_{pi}} \end{gathered} \tag{11}$$

$$P = \rho_g R T_g \tag{12}$$

With the input upper index *j* by the system of equations (5-12) we describe the possible cases of two-measure jets: at *j* =0 flat jets and at *j* =1 axial-symmetric. The lower indexes *g* and *p* refer to the gas phase and the phase of the admixtures accordingly. The used two-fluid method allows reading of the forces of the interphase interaction *Fi*, by which the equations for movement of the two phases are connected. In this case of two-phase non-isothermal jet the forces of the interphase interaction are presented with the following sum:

$$\sum_{i=1}^{N} \vec{F}_i = \vec{f}_A + \vec{f}_M + \vec{f}_S + \vec{f}_{TM} + \vec{f}_\phi + \vec{f}_G \tag{13}$$

where: $\vec{f}_A = 0.5 C_R S \rho_g \left| \vec{V}_r \right| \vec{V}_r$ - is the drag force, $\vec{f}_M = K_M \rho_g D_p^3 \vec{\Omega}_r$ - is the Magnus' force, $\vec{f}_s = K_s \nu^{0.5} \rho_g D_p^2 \left(U_g - U_p \right) \left(\partial U_g / \partial y \right)^{0.5}$ - is the Safman's force, $\vec{f}_{TM} = 0.5 m_p \overline{\partial V_p'^2} / \partial y$ - is the force of turboforese, $\vec{f}_T = -4.5 \nu \left(\rho_g / T_g \right) D_p \lambda_g / \left(2\lambda_g + \lambda_p \right) \Delta T_g$ - is the force of thermoforese, $\vec{f}_\Phi = (\pi / 6) \rho_p D_p^3 q E$ is the force from photoforese, $\vec{f}_g$ - is the mass force [7,8], C $\vec{V}_r = \vec{V}_g - \vec{V}_p$ is the relative velocity, $\vec{\Omega}_r = \vec{\omega}_g - \vec{\Omega}_p$ - the relative whirl of the velocity, C_R, K_M, K_g - invariable, q - electrical charge of the particles, E – voltage of the electric field.

The enthalpy of the gas phase and the admixtures of the non-isothermal turbulent jets is defined by the following equations:

$$h_g = C_{pg} \left(T_g - T_2 \right), h_p = C_{pp} \left(T_p \right) \tag{14}$$

Where : - specific thermal capacity at constant pressure for the gas phase and for the admixtures, T_g, T_p and T_2 - temperature of the gas phase, the admixtures and the environment, $a,b,a^{/},b^{/}$ - constant in the equations for the gas phase and for the admixtures:

The thermal interaction between the phases is defined by

$$Q=6Nu\lambda\left(D_p\right)^{-2}\left(T_g-T_p\right)_t \qquad (15)$$

Where $Nu=2+CRe_p^nP_t^m$, the invariables C,n,m depend on Re_p.

II. Turbulence model

The binary correlations of velocity, density and temperature also take part in the movement equations. They can be described by the turbulence viscosity and the field of the averaged parameters:

Sc_t,Pr_t - Schmidt and Prandtl turbulence numbers.

The observed model of turbulence in [1,2] and improved in [4] we make the following modification: For closing the system of equations, which describe the spreading of the non-isothermal nano-jet, we apply a turbulence model with two equations for the transfer of pulsing energy of the gas phase and the admixtures, and one for the dissipation velocity of the pulsation energy, called $\kappa_g-\kappa_p-\varepsilon$. This model was successfully used up to now in our solutions for isothermal jets [4, 10, 11], as we have added its application for one much more sophisticated case – spreading of non-isothermal two-phase nano-jet. The next described modification of the model can be applied also at two-phase jets in channels, if the corresponding boundary conditions are observed, as well as if the thermal and mass-exchange processes in the wall boundary layer are observed. We have to emphasize that the its very application in this case does not decrease the aggregation of the suggested turbulence model.

The suggested turbulence model is described with the following equations:

$$\begin{aligned} &y\rho_g U_g\frac{\partial k_g}{\partial x}+y\rho_g V_g\frac{\partial k_g}{\partial y}=\partial/\partial y\left[\left(y\rho_g\nu_{tg}\right)/\sigma_k.\left(\partial k_g/\partial y\right)\right]+\\ &+y\rho_g\nu_{tg}\left(\partial U_g/\partial y\right)^2-y\rho_g\left(\varepsilon+\varepsilon_p\right) \end{aligned} \qquad (16)$$

$$\begin{aligned} &y^j\rho_p U_p\frac{\partial k_p}{\partial x}+y^j\rho_p V_p\partial k_p/\partial y=\partial/\partial y\left[\left(y^j\rho_p\nu_{tp}\right)/\sigma_k.\left(\partial k_p/\partial y\right)\right]+\\ &+y^j\rho_p\nu_{tp}\left(\partial U_p/\partial y\right)^2-y^j\rho_p\varepsilon_p^* \end{aligned} \qquad (17)$$

$$\begin{aligned} &y\rho_g U_g\frac{\partial\varepsilon}{\partial x}+y\rho_g V_g\partial\varepsilon/\partial y=\partial/\partial y\left[\left(y\rho_g\nu_{tg}\right)/\sigma_\varepsilon\left(\frac{\partial\varepsilon}{\partial y}\right)\right]-\\ &-y\rho_g\Phi_p+y\rho_g C_{\varepsilon1}/k_g[\nu_{tg}\left(\frac{\partial U_p}{\partial y}\right)^2+G]-y\rho_g\varepsilon/k_g\left(C_{\varepsilon2}-C_{\varepsilon3}\chi\right) \end{aligned} \qquad (18)$$

III. Characteristic equation

The system of differential equations is reduced to one characteristic equation of the following type:

$$A.\partial Z/\partial x+B.\partial Z/\partial y=C.\partial^2 Z/\partial y^2+D \qquad (19)$$

Where Y, A, B, C и D are reduced variables and values.

For solving of the problem we apply explicit method in end differences, as we use Du Fort – Frankel scheme. We define values of the parameters in i-section of the known (or calculated) values in two preceding sections – i-1 и i-2

$$Z_{i,j}=E_2/E_1.Z_{i-1,j}\ +E_3/E_1.Z_{i-1,j+1}\ +E_4/E_1.Z_{i-1,j-1}\ +E_5/E_1 \qquad (20)$$

The code is developed using program language PASCAL and is constructed on a module principle. A special subroutine is developed for input data.

IV. Analysis of the results

On figures 1 to 13 we have the results from three studied regimes. χ_0=0,7; 0,977; dp=50; 250; 500.10^{-9}m;

Ug_0=26,52m/s; 52,6m/s; Up_0=26,52m/s; 52,6m/s T_2=293K

The alteration of the mass concentration of admixtures is shown on Fig. 5, 8 and 13 for the corresponding regimes.

We can follow up the alteration of the concentration distribution of admixtures when the velocity of flowing and the initial concentration are altered.

We can see on Fig. 14 and 15 the slackening of the velocities of the two phases in different regimes. The slackening of the gas phase velocity has a bigger gradient, compared to the slackening velocity of the admixtures.

$$\overline{V_V} = \frac{V_V}{u_0}$$

$$d_p = 50,250,500.10^{-9}\,m$$

$$\rho_p = 10^3\,kg/m^3 \quad \rho_g = 1,2\,kg/m^3 .$$

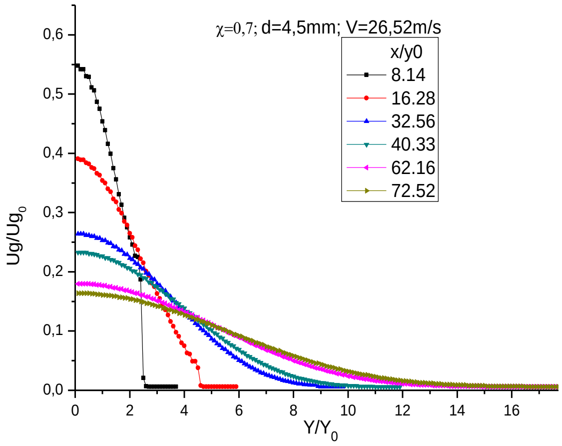


Fig.1 *Distributing of the carrier phase Ug at χ=0,7, V=26,52m/s*

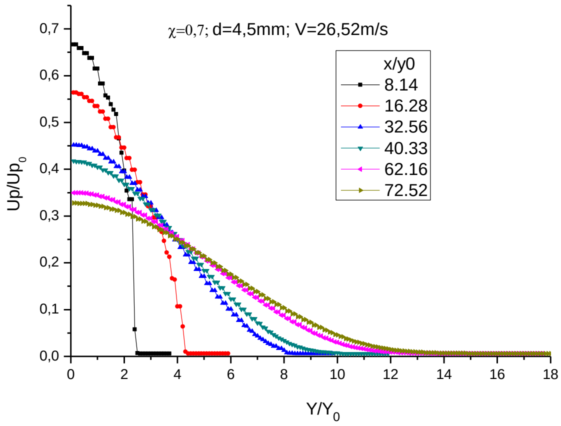


Fig.2 *Distributing of the admixture Up at χ=0,7, V=26,52m/s*

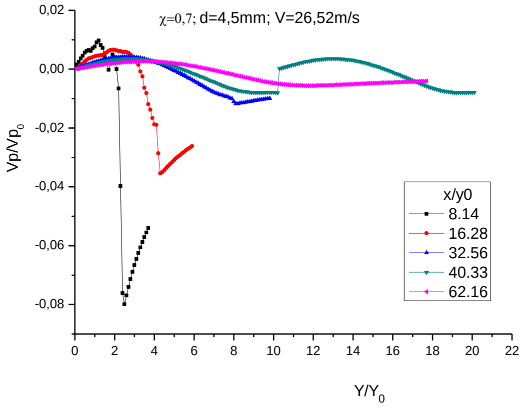


Fig.3 *Alteration of the cross component of the Vp at χ=0,7, V=26,52m/s*

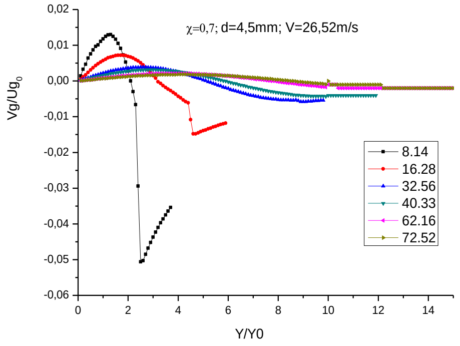


Fig.4 *Alteration of Vg at χ=0,7, V=26,52m/s*

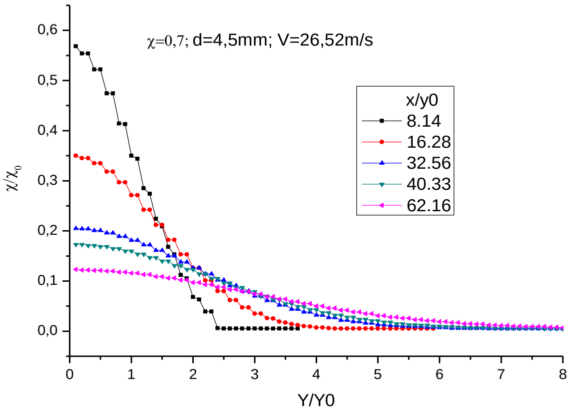


Fig.5 *Alteration of the admixture concentration χ at χ=0,7, V=26,52m/s*

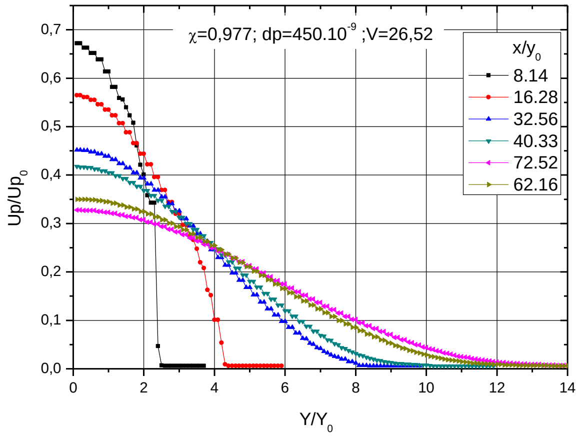


Fig.6 *Alteration of the admixture velocity Up at χ=0,977, V=26,52m/s*

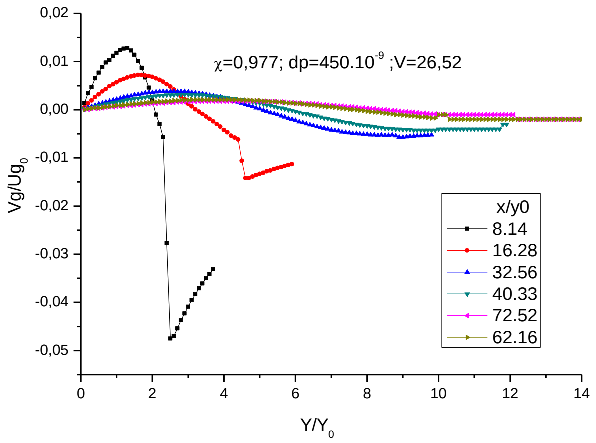


Fig.7 *Alteration of the cross component of the carrier phase Vg at χ=0,977, V=26,52m/s*

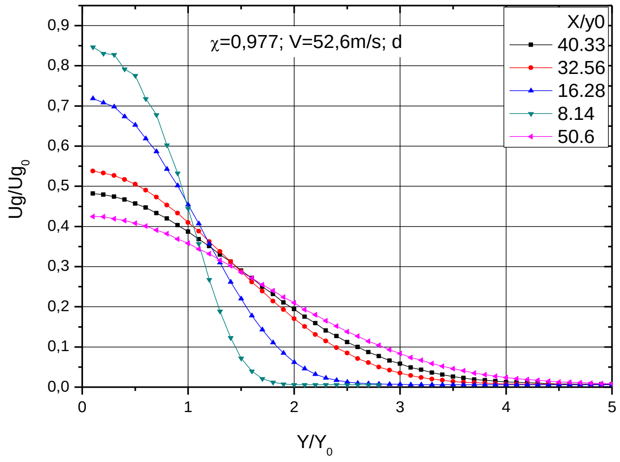


Fig.10 *Alteration of the velocity of the carrier phase Ug at χ=0,977, V=52,6m/s*

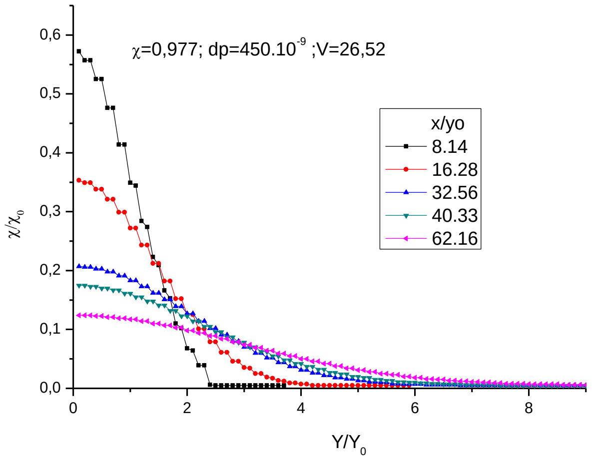


Fig.8 *Alteration of the concentration of the admixture χ at χ=0,977, V=26,52m/s*

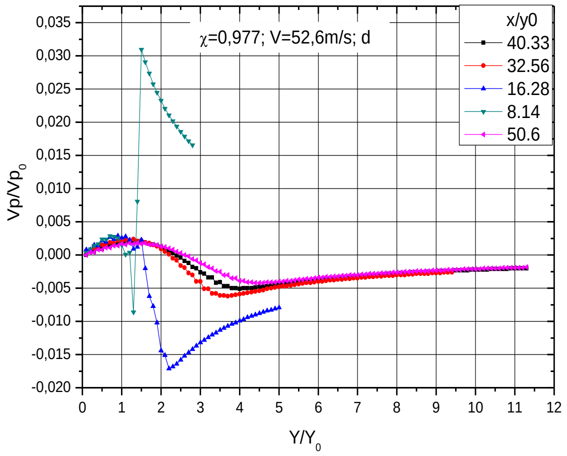


Fig.11 *Alteration of the cross component of the Vp at χ=0,977, V=52,6m/s*

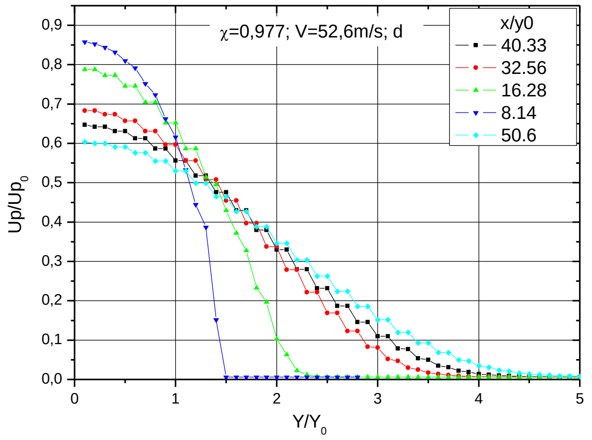


Fig.9 *Alteration of the velosity of the admixture Up at χ=0,977, V=52,6m/s*

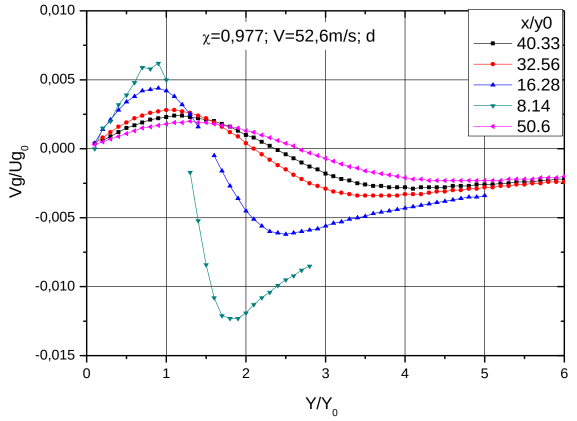


Fig.12 *Alteration of the cross component Vg at χ=0,977, V=52,6m/s*

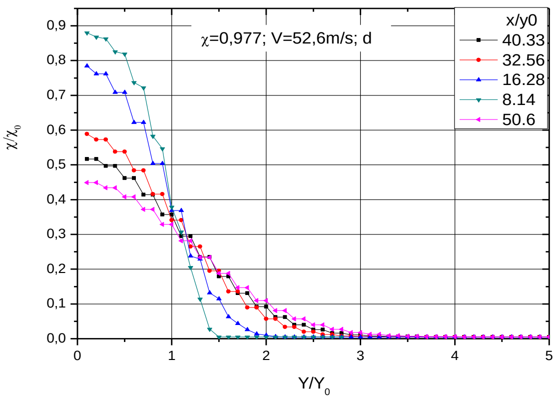


Fig.13 *Alteration of the concentration of the admixture χ at χ=0,977, V=52,6m/s*

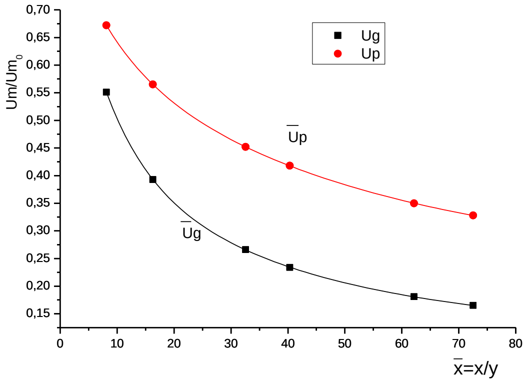
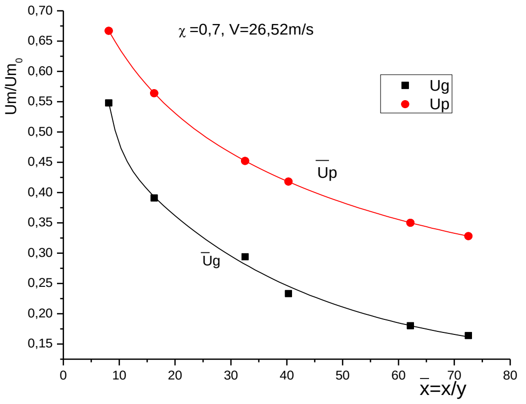


Fig. 14 *Slackening of the velocity of the carrier phase and the phase of the admixture in flow direction at initial concentration χ=0,977, V=26,52m/s*



[1]

Fig. 15 *Slackening of the velocity of the carrier phase and the phase of the admixture in flow direction at initial concentration χ=0,7, V=26,52m/s*

V. Conclusion

The first model studies of spreading of nano-jets show the applicability of the developed mathematical model for the definition of the main parameters of the flow. Practically, we can foresee the slacking of the particles velocity in flow direction, as well as the spreading of the admixtures in separate sections of the flow. This study method can be used also in channel flows when the initial and boundary conditions are changed.

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NUMERICAL ANALYSIS OF TWO-PHASE NON-ISOTHERMAL NANO JETS

M. S. Angelov[1], I. S. Antonov[2], D. P. Stoeva[1], P.R.Rainov[1]

[1]*University of Food Technologies 26, Maritza Blvd., 4002 Plovdiv*
[2]*Technical University of Sofia*

Abstract: *The choice of suitable mathematical model and corresponding model of turbulent shear stresses is a very important issue while analyzing turbulent two-phase nano jets. We accept two-fluid scheme of the jet, according to which in every point of the area and in every moment, both phases have different densities, velocities and temperatures. The relation between phases in the equations for movement and heat transfer are the powers of phase interaction, which are accepted to be essential for the corresponding jet. For closing the equation system for movement, we apply one modification of the* $\kappa-\varepsilon$ *model of turbulence. It uses two equations for the turbulent kinetic energy for the phases and one for the dissipation of turbulent kinetic energy of the carrier phase* $\kappa_g-\kappa_p-\varepsilon$ *model.*

Keywords: turbulent two-phase nano jets, $\kappa_g-\kappa_p-\varepsilon$ model, numerical analysis

I. Introduction

The two-phase character of the jet influences the fixation of equations for turbulent energy and dissipation of turbulent energy by adding additional dissipative terms. One of the accurate methods for describing heterogeneous dispersed two-phase environments is based on the concept of multi velocity interpenetrating continuum. We take for granted the existence of various fields of the velocities, temperatures and densities of the phases - a carrier phase and a phase of the admixtures. The phases have their own velocity, density and temperature in every point of the jet. The object of the research is numerical modeling of two-phase non-isothermal turbulent nano jet, which flows into still environment from the carrier phase with different temperature, compared to the temperature of the nano-jet.

Many modern technologies and apparatus require the dispersion of tiny quantities of fluids. Such necessity appears when there is a requirement for very fast evaporation of cryogenic fluids in special equipment for generating aerosols or mist in a particular space in order to increase the moisture content of the air (in fire-fighting devices, air handling units, when spreading liquid medicines), by obtaining pure substances in laboratory conditions.

For achieving of very thin dispersion at the level of nanoparts or micrometers ($d_p \leq 10\div20\mu m$), a very small flow rate is used – about Q=5÷10 *l*/h and the dimension of the nozzle unit, from which the jet comes, is recommended to be about $d_д \approx 0,25\div5$mm. The use of ultrasonic emitter, piezoelectric effect and others are recommended for use when thing dispersion is required. For example, if we have dispersed liquid drops with radius $d_p=10\mu m$, if we use electrical charge E=300V, the drops are destroyed under the power of the aerodynamic forces and the radius of the newly formed drops [1] is five times smaller $r = 2.10^{-6}$m. If we increase the charge to E=350V the radius decreases to $r = 892.10^{-9}$ m and at E=400V then $r = 0,4.10^{-6}$m (400.10^{-9} m). We can conclude by this method of dispersion that by increasing the electrical charge we can successfully decrease the dimension of the finely dispersed drops.

In many cases it is of particular importance to leaving the finely dispersed liquid droplets in a state of hovering. It is known that this condition occurs when the force of its own weight $\overrightarrow{f_g}$ is balanced or is lower than the aerodynamic resistance of the free falling of the droplet or the particle $\overrightarrow{f_R}$,as:

$$\overrightarrow{f_g}=\vec{g}.m_p \tag{1}$$

$$\overrightarrow{f_R}=C_R.S.\rho_g\frac{V_{cn}^2}{2} \tag{2}$$

where: m_p - the mass of the particle $m_p=\rho_p.W$ - density of the particle volume; C_R - aerodynamic resistance coefficient; S - area of the middle section of the droplet, ρ_p and ρ_g - density of the admixtures and the gas air environment; V_{cn} - free falling, resp. $V_{cn}=V_V$; V - velocity of hovering. Equalizing both forces in (1) and (2) the result is the of hovering, if it is considered lower than the velocity of free falling ($V_V<V_{cn}$) will be

$$V_V\leq\sqrt{\frac{2gm_p}{C_RS\rho_g}} \tag{3}$$

As the Reynolds number of admixtures $Re_p = \frac{V_r.d_p}{\nu}$ (when $V_r = V_g - V_p$, d_p-diameter of the admixture particle viscosity of the gas environment) is always lower than one at level of nano particles ($Re_p < 1$), then the coefficient C_R is calculated by the Stoke's law:

The essential question, arising from the movement of droplets of nano-parts level is: Where is point in which the hovering velosity will be reached? This means at what level x from the outgoing nozzle the velocity of the nano-particle will reach V_V. In order to achieve the necessary information, the flow must be studied as a movement of two-phase mixture, on which the two-phase model is applied, as described in [2] and [3].

I. Basic equations for movement

The two-phase axial-symmetric non-isothermal non-jet is described in Decartes coordinate system of equations:

$$C_R = \frac{24}{Re_p} \tag{4}$$

$$\partial / \partial \mathrm{x} \left[\mathrm{y}^{\mathrm{j}} \mathrm{U}_{\mathrm{g}} \rho_{\mathrm{g}}\right] + \partial / \partial \mathrm{y} \left[\mathrm{y}^{\mathrm{j}} \mathrm{V}_{\mathrm{g}} \rho_{\mathrm{g}}\right] = 0 \tag{5}$$

$$\partial / \partial \mathrm{x} \left[\mathrm{y}^{\mathrm{j}} \mathrm{U}_{\mathrm{p}} \rho_{\mathrm{p}}\right] + \partial / \partial \mathrm{y} \left[\mathrm{y}^{\mathrm{j}} \mathrm{V}_{\mathrm{p}} \rho_{\mathrm{p}}\right] = 0 \tag{6}$$

$$\left[\mathrm{y}^{\mathrm{j}} \mathrm{U}_{\mathrm{p}}\right] \partial \rho_{\mathrm{p}} / \partial \mathrm{x} + \left[\mathrm{y}^{\mathrm{j}} \mathrm{V}_{\mathrm{p}}\right] \partial \rho_{\mathrm{p}} / \partial \mathrm{y} = -\partial / \partial \mathrm{y} \left[\mathrm{y}^{\mathrm{j}} \overline{\rho'_{\mathrm{p}} \mathrm{V}'_{\mathrm{p}}}\right] - \overline{\rho'_{\mathrm{p}} \mathrm{V}'_{\mathrm{p}}} \tag{7}$$

$$\left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \mathrm{U}_{\mathrm{g}}\right] \partial \mathrm{U}_{\mathrm{g}} / \partial \mathrm{x} + \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \mathrm{V}_{\mathrm{g}}\right] \partial \mathrm{U}_{\mathrm{g}} / \partial \mathrm{y} = -\partial / \partial \mathrm{y} \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \overline{\mathrm{U}'_{\mathrm{g}} \mathrm{V}'_{\mathrm{g}}}\right] - \mathrm{F}_{\mathrm{x}} \mathrm{y}^{\mathrm{j}} \tag{8}$$

$$\begin{gathered} \left[y^j \rho_p u_p \right] \partial u_p / \partial x + \left[y^j (\rho_p V_p + \overline{\rho'_p V'_p}) \right] \partial U_p / \partial y = \\ = -\partial / \partial y \left[y^j \rho_p \overline{U'_p V'_p} \right] + F_x y^j \end{gathered} \tag{9}$$

$$\begin{gathered} \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{p}} \mathrm{U}_{\mathrm{p}}\right] \partial \mathrm{h}_{\mathrm{p}} / \partial \mathrm{x} + \left[\mathrm{y}^{\mathrm{j}} (\rho_{\mathrm{p}} \mathrm{V}_{\mathrm{p}} + \overline{\rho'_{\mathrm{g}} \mathrm{V}'_{\mathrm{g}}})\right] \partial \mathrm{h}_{\mathrm{p}} / \partial \mathrm{x} = \\ = -\partial / \partial \mathrm{y} \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{p}} \overline{\mathrm{h}'_{\mathrm{p}} \mathrm{V}'_{\mathrm{p}}}\right] + \mathrm{Q} \mathrm{y}^{\mathrm{j}} \end{gathered} \tag{10}$$

$$\begin{gathered} \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \mathrm{U}_{\mathrm{g}}\right] \partial \mathrm{h}_{\mathrm{g}} / \partial \mathrm{x} + \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \mathrm{V}_{\mathrm{g}}\right] \partial \mathrm{h}_{\mathrm{g}} / \partial \mathrm{x} = -\partial / \partial \mathrm{y} \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \overline{\mathrm{h}'_{\mathrm{g}} \mathrm{V}'_{\mathrm{g}}}\right] - \\ - \left[\mathrm{y}^{\mathrm{j}} \rho_{\mathrm{g}} \overline{\mathrm{h}'_{\mathrm{g}} \mathrm{V}'_{\mathrm{g}}}\right] \partial \mathrm{U}_{\mathrm{g}} / \partial \mathrm{y} - \mathrm{Q} \mathrm{y}^{\mathrm{j}} + \mathrm{F}_{\mathrm{x}} \mathrm{y}^{\mathrm{j}} \left(\mathrm{U}_{\mathrm{g}} - \mathrm{U}_{\mathrm{p}}\right) + \mathrm{F}_{\mathrm{y}} \mathrm{y}^{\mathrm{j}} \left(\mathrm{V}_{\mathrm{g}} - \mathrm{V}_{\mathrm{p}}\right) - \\ - \sum_{\mathrm{i}=1}^{3} \overline{\mathrm{F}'_{\mathrm{i}} \mathrm{V}'_{\mathrm{pi}}} \end{gathered} \tag{11}$$

$$\mathrm{P} = \rho_{\mathrm{g}} \mathrm{R} \mathrm{T}_{\mathrm{g}} \tag{12}$$

With the input upper index *j* by the system of equations (5-12) we describe the possible cases of two-measure jets: at *j* =0 flat jets and at *j* =1 axial-symmetric. The lower indexes *g* and *p* refer to the gas phase and the phase of the admixtures accordingly. The used two-fluid method allows reading of the forces of the interphase interaction *Fi*, by which the equations for movement of the two phases are connected. In this case of two-phase non-isothermal jet the forces of the interphase interaction are presented with the following sum:

$$\sum_{\mathrm{i}=1}^{\mathrm{N}} \vec{\mathrm{F}}_{\mathrm{i}} = \vec{\mathrm{f}}_{\mathrm{A}} + \vec{\mathrm{f}}_{\mathrm{M}} + \vec{\mathrm{f}}_{\mathrm{S}} + \vec{\mathrm{f}}_{\mathrm{TM}} + \vec{\mathrm{f}}_{\phi} + \vec{\mathrm{f}}_{\mathrm{G}} \tag{13}$$

where: $\vec{\mathrm{f}}_{\mathrm{A}} = 0.5 \mathrm{C}_{\mathrm{R}} \mathrm{S} \rho_{\mathrm{g}} \left|\vec{\mathrm{V}}_{\mathrm{r}}\right| \vec{\mathrm{V}}_{\mathrm{r}}$ - is the drag force, $\vec{\mathrm{f}}_{\mathrm{M}} = \mathrm{K}_{\mathrm{M}} \rho_{\mathrm{g}} \mathrm{D}_{\mathrm{p}}^{3} \vec{\Omega}_{\mathrm{r}}$ - is the Magnus' force, $\vec{\mathrm{f}}_{\mathrm{s}} = \mathrm{K}_{\mathrm{s}} \nu^{0.5} \rho_{\mathrm{g}} \mathrm{D}_{\mathrm{p}}^{2} \left(\mathrm{U}_{\mathrm{g}} - \mathrm{U}_{\mathrm{p}}\right) \left(\partial \mathrm{U}_{\mathrm{g}} / \partial \mathrm{y}\right)^{0.5}$ - is the Safman's force, $\vec{\mathrm{f}}_{\mathrm{TM}} = 0.5 \mathrm{m}_{\mathrm{p}} \overline{\partial} \overline{\mathrm{V}}_{\mathrm{p}}'^{2} / \partial \mathrm{y}$ - is the force of turboforese, $\vec{\mathrm{f}}_{\mathrm{T}} = -4.5 \nu \left(\rho_{\mathrm{g}} / \mathrm{T}_{\mathrm{g}}\right) \mathrm{D}_{\mathrm{p}} \lambda_{\mathrm{g}} / \left(2 \lambda_{\mathrm{g}} + \lambda_{\mathrm{p}}\right) \Delta \mathrm{T}_{\mathrm{g}}$ - is the force of thermoforese , $\vec{\mathrm{f}}_{\Phi} = (\pi / 6) \rho_{\mathrm{p}} \mathrm{D}_{\mathrm{p}}^{3} \mathrm{q} \mathrm{E}$ is the force from photoforese, $\vec{\mathrm{f}}_{\mathrm{g}}$ - is the mass force [7,8], C $\vec{V}_r = \vec{V}_g - \vec{V}_p$ is the relative velocity, $\vec{\Omega}_r = \vec{\omega}_g - \vec{\Omega}_p$ - the relative whirl of the velocity, C_R, K_M, K_g - invariable, q - electrical charge of the particles, E – voltage of the electric field.

The enthalpy of the gas phase and the admixtures of the non-isothermal turbulent jets is defined by the following equations:

$$h_g = C_{pg} \left(T_g - T_2\right), h_p = C_{pp} \left(T_p\right) \tag{14}$$

Where : - specific thermal capacity at constant pressure for the gas phase and for the admixtures, T_g, T_p and T_2 - temperature of the gas phase, the

admixtures and the environment, $a,b,a^{/},b^{/}$ - constant in the equations for the gas phase and for the admixtures:
The thermal interaction between the phases is defined by

$$Q=6Nu\lambda\left(D_p\right)^{-2}\left(T_g-T_p\right)_t \tag{15}$$

Where $Nu=2+CRe_p^nP_t^m$, the invariables C,n,m depend on Re_p.

II. Turbulence model

The binary correlations of velocity, density and temperature also take part in the movement equations. They can be described by the turbulence viscosity and the field of the averaged parameters:
Sc_t,Pr_t - Schmidt and Prandtl turbulence numbers.

The observed model of turbulence in [1,2] and improved in [4] we make the following modification: For closing the system of equations, which describe the spreading of the non-isothermal nano-jet, we apply a turbulence model with two equations for the transfer of pulsing energy of the gas phase and the admixtures, and one for the dissipation velocity of the pulsation energy, called $\kappa_g-\kappa_p-\varepsilon$. This model was successfully used up to now in our solutions for isothermal jets [4, 10, 11], as we have added its application for one much more sophisticated case – spreading of non-isothermal two-phase nano-jet. The next described modification of the model can be applied also at two-phase jets in channels, if the corresponding boundary conditions are observed, as well as if the thermal and mass-exchange processes in the wall boundary layer are observed. We have to emphasize that the its very application in this case does not decrease the aggregation of the suggested turbulence model.

The suggested turbulence model is described with the following equations:

$$\begin{aligned}&y\rho_g U_g\frac{\partial k_g}{\partial x}+y\rho_g V_g\frac{\partial k_g}{\partial y}=\partial/\partial y\left[\left(y\rho_g\nu_{tg}\right)/\sigma_k.\left(\partial k_g/\partial y\right)\right]+\\&+y\rho_g\nu_{tg}\left(\partial U_g/\partial y\right)^2-y\rho_g\left(\varepsilon+\varepsilon_p\right)\end{aligned} \tag{16}$$

$$\begin{aligned}&y^j\rho_p U_p\frac{\partial k_p}{\partial x}+y^j\rho_p V_p\partial k_p/\partial y=\partial/\partial y\left[\left(y^j\rho_p\nu_{tp}\right)/\sigma_k.\left(\partial k_p/\partial y\right)\right]+\\&+y^j\rho_p\nu_{tp}\left(\partial U_p/\partial y\right)^2-y^j\rho_p\varepsilon_p^*\end{aligned} \tag{17}$$

$$\begin{aligned}&y\rho_g U_g\frac{\partial\varepsilon}{\partial x}+y\rho_g V_g\partial\varepsilon/\partial y=\partial/\partial y\left[\left(y\rho_g\nu_{tg}\right)/\sigma_\varepsilon\left(\frac{\partial\varepsilon}{\partial y}\right)\right]-\\&-y\rho_g\Phi_p+y\rho_g C_{\varepsilon1}/k_g[\nu_{tg}\left(\frac{\partial U_p}{\partial y}\right)^2+G]-y\rho_g\varepsilon/k_g\left(C_{\varepsilon2}-C_{\varepsilon3}\chi\right)\end{aligned} \tag{18}$$

III. Characteristic equation

The system of differential equations is reduced to one characteristic equation of the following type:

$$A.\partial Z/\partial x+B.\partial Z/\partial y=C.\partial^2Z/\partial y^2+D \tag{19}$$

Where Y, A, B, C и D are reduced variables and values.

For solving of the problem we apply explicit method in end differences, as we use Du Fort – Frankel scheme. We define values of the parameters in i-section of the known (or calculated) values in two preceding sections – i-1 и i-2

$$Z_{i,j}=E_2/E_1.Z_{i-1,j}\ +E_3/E_1.Z_{i-1,j+1}\ +E_4/E_1.Z_{i-1,j-1}\ +E_5/E_1 \tag{20}$$

The code is developed using program language PASCAL and is constructed on a module principle. A special subroutine is developed for input data.

IV. Analysis of the results

On figures 1 to 13 we have the results from three studied regimes. χ_0=0,7; 0,977; dp=50; 250; 500.10^{-9}m;
Ug$_0$=26,52m/s; 52,6m/s; Up$_0$=26,52m/s; 52,6m/s T$_2$=293K

The alteration of the mass concentration of admixtures is shown on Fig. 5, 8 and 13 for the corresponding regimes.

We can follow up the alteration of the concentration distribution of admixtures when the velocity of flowing and the initial concentration are altered.

We can see on Fig. 14 and 15 the slackening of the velocities of the two phases in different regimes. The slackening of the gas phase velocity has a bigger gradient, compared to the slackening velocity of the admixtures.

$$\overline{V_V} = \frac{V_V}{u_0}$$

$$d_p = 50,250,500.10^{-9} m$$

$$\rho_p = 10^3 \, kg/m^3 \quad \rho_g = 1,2 \, kg/m^3 .$$

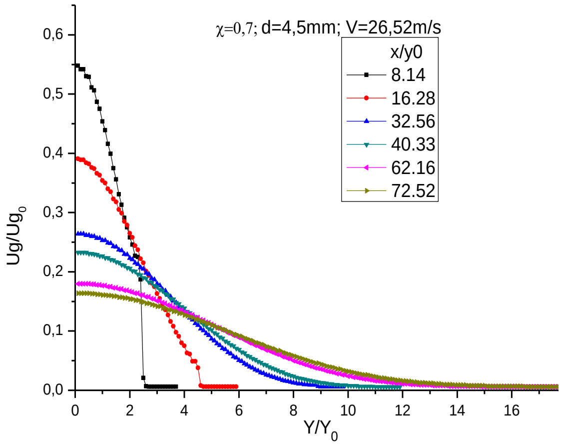


Fig.1 *Distributing of the carrier phase Ug at χ=0,7, V=26,52m/s*

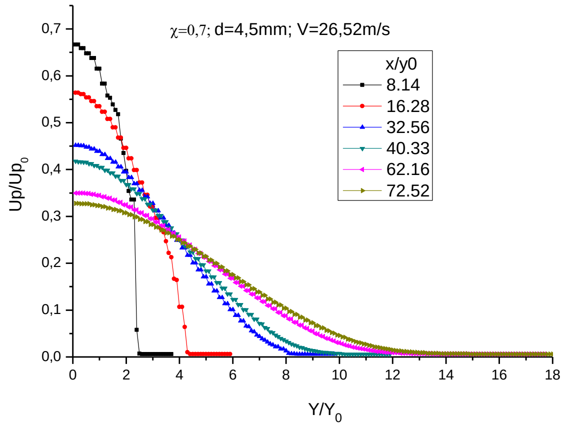


Fig.2 *Distributing of the admixture Up at χ=0,7, V=26,52m/s*

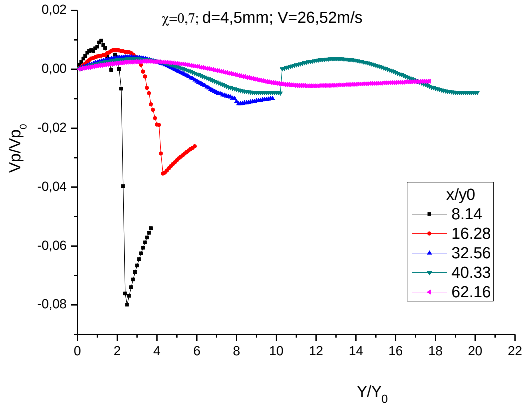


Fig.3 *Alteration of the cross component of the Vp at χ=0,7, V=26,52m/s*

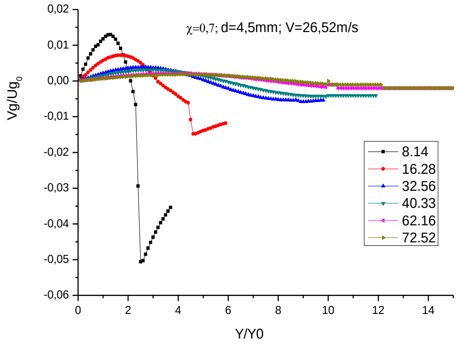


Fig.4 *Alteration of Vg at χ=0,7, V=26,52m/s*

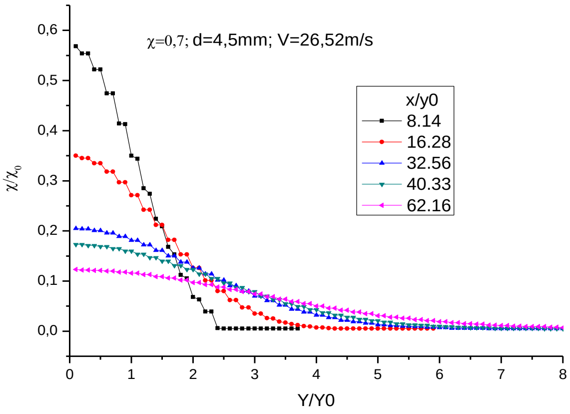


Fig.5 *Alteration of the admixture concentration χ at χ=0,7, V=26,52m/s*

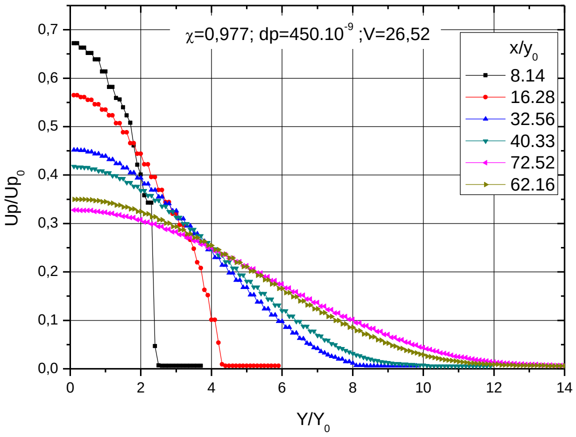


Fig.6 *Alteration of the admixture velocity Up at χ=0,977, V=26,52m/s*

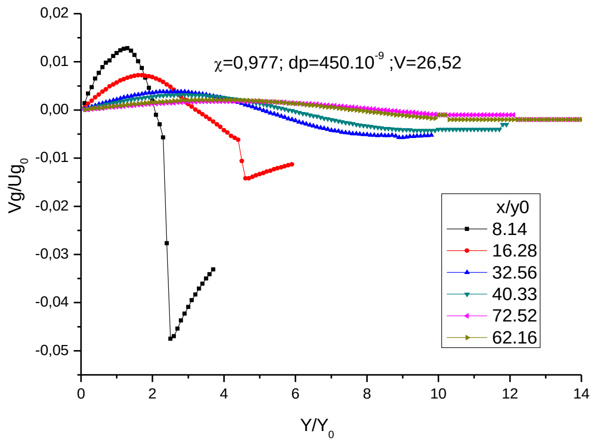


Fig.7 *Alteration of the cross component of the carrier phase Vg at* $\chi=0{,}977$*, V=26,52m/s*

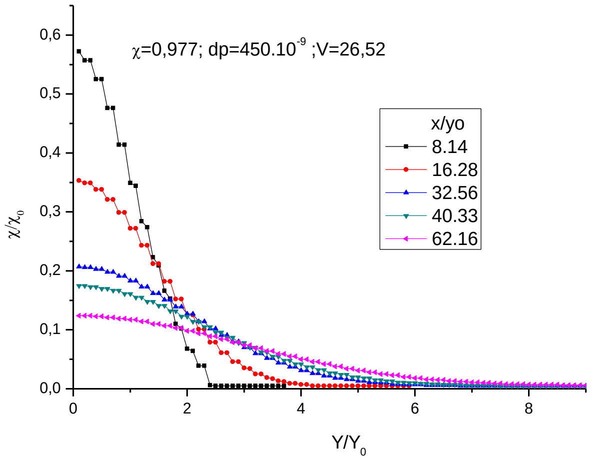


Fig.8 *Alteration of the concentration of the admixture* χ *at* $\chi=0{,}977$*, V=26,52m/s*

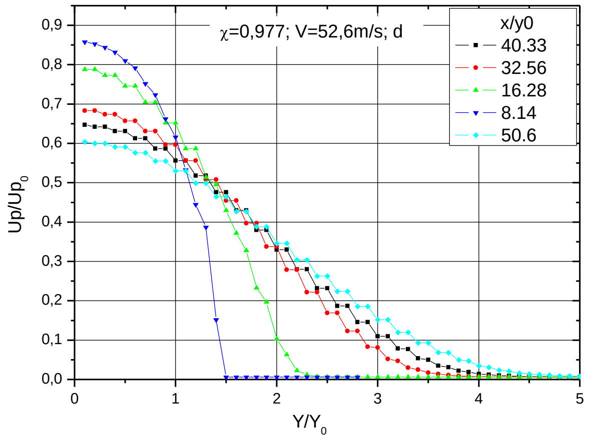


Fig.9 *Alteration of the velosity of the admixture Up at* $\chi=0{,}977$*, V=52,6m/s*

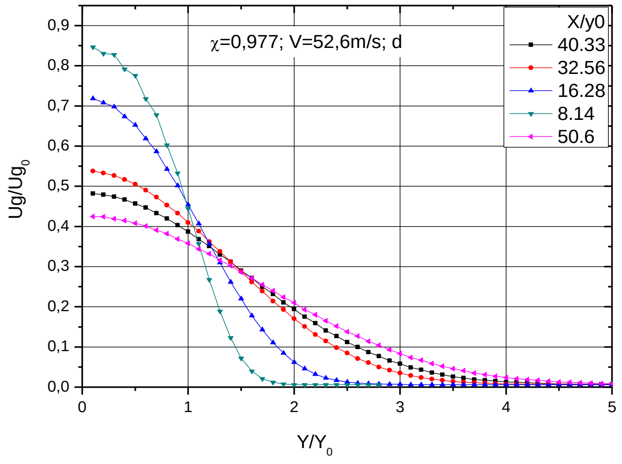


Fig.10 *Alteration of the velocity of the carrier phase Ug at* $\chi=0{,}977$*, V=52,6m/s*

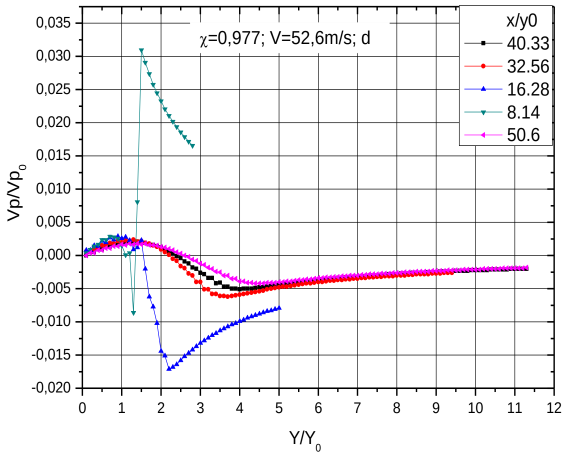


Fig.11 *Alteration of the cross component of the Vp at* $\chi=0{,}977$*, V=52,6m/s*

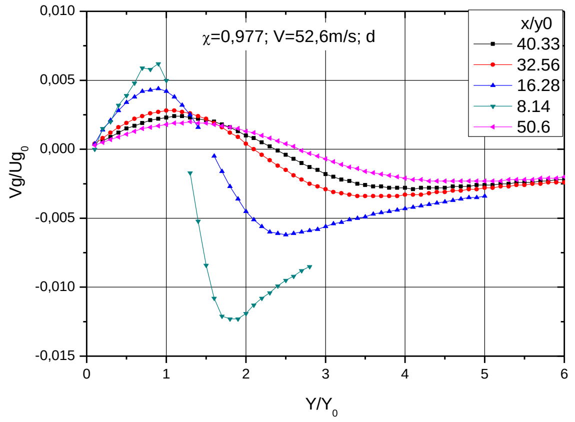


Fig.12 *Alteration of the cross component Vg at* $\chi=0{,}977$*, V=52,6m/s*

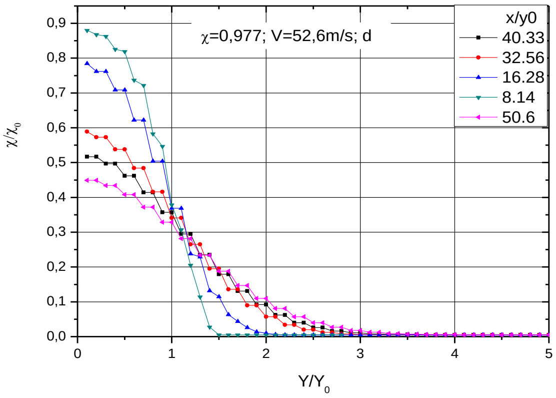


Fig.13 *Alteration of the concentration of the admixture χ at χ=0,977, V=52,6m/s*

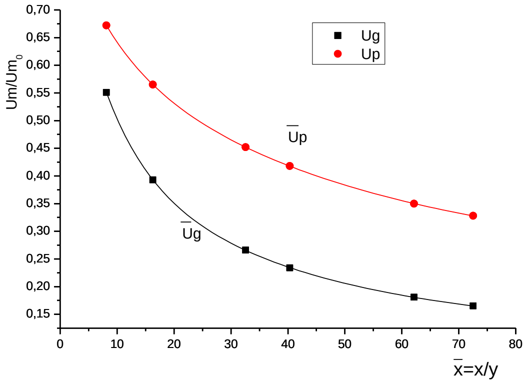
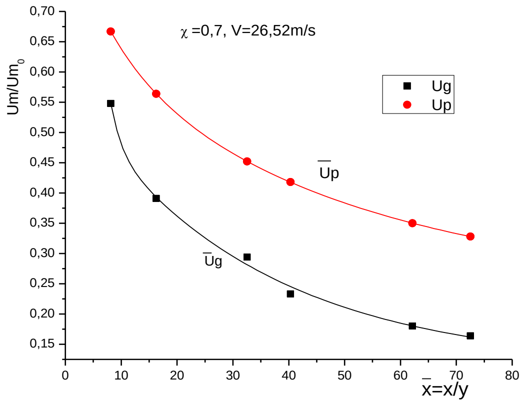


Fig. 14 *Slackening of the velocity of the carrier phase and the phase of the admixture in flow direction at initial concentration χ=0,977, V=26,52m/s*



[1]

Fig. 15 *Slackening of the velocity of the carrier phase and the phase of the admixture in flow direction at initial concentration χ=0,7, V=26,52m/s*

V. Conclusion

The first model studies of spreading of nano-jets show the applicability of the developed mathematical model for the definition of the main parameters of the flow. Practically, we can foresee the slacking of the particles velocity in flow direction, as well as the spreading of the admixtures in separate sections of the flow. This study method can be used also in channel flows when the initial and boundary conditions are changed.

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The intensification of saturation process of carbonated beverages by using artificial hydrodynamic cavitation

Ruslan Petrikei

National University of Food Technologies, Kyiv, Ukraine

Abstract. *The work of cavitation devices based on the use of artificial hydrodynamic cavitation phenomenon that occurs during saturation drinks by gaseous CO2 stream and promotes intensification of carbonation were studied. The influence of basic and additional factors on the process of saturation drinks was analyzed. According to the research results the optimal cavitation device for beverage CO2 saturation in the flow was selected.*

Key words: carbon dioxide, drink, saturation, intensification, hydrodynamic, cavitation, synchronous.

I. Introduction

In a market economy and the continuous development of technology extremely high requirements to the food quality, which primarily depends on the raw materials, the type of manufacturing and using equipment set. One of the major factors that contribute to improving the quality of carbonated beverages is the quality of their saturation with carbon dioxide (CO_2). Since the carbonation process is the final stage of carbonated beverages production, its implementation primarily depends on: 1) the visual appeal of beverages, 2) organoleptic indicators; 3) drinks storage life.

For the carbonation of beverages a large number of absorption equipment which may not always provide the highest quality and efficiency of saturation beverage process is used. So the development of a new device for the carbonation of beverages that will provide all the technical and technological requirements and savings in carbon dioxide is really urgent. The hydrodynamic cavitations devices used for the treatment of liquid and gas-liquid medium in the flow, meet fully these conditions. The high quality of the finished product is achieved by hydrodynamic cavitation favorable action on the treated product.

Cavitational devices did not find adequate implementation in the industry because of insufficient study of these devices. Therefore, research of beverages carbonation process with using cavitation devices is an actual task.

II. Result and discussion

V. Stabnikov's theory about the surface updates of conduct phases gives a complete picture of the mechanism of carbonation of beverages in the flow. Its essence is based on the fact that in the overall mass transfer the reformed surface contacts of phases with elements that have not participated in diffusion yet, play a crucial role. The surface is updated as a result of entry into the interface of turbulent eddies that reveal new layers contacting media, which leads to the formation of new contact surfaces of phases [4].

The most intensive new contact surface phases forms during cavitation phenomena. Hydrodynamic cavitation may occur: 1) when the fluid moves through the local constriction of the pipeline, 2) at the site of rupture of fluid flow through the installation on its way static cavitators 3) due to the forced introduction of fluid into the main stream of fluid (artificial hydrodynamic cavitation).

Most of the models, explaining the mechanism of cavitation, are based on a cumulative hypothesis. According to it, the process of cavitation effect is associated mainly with the formation of cumulative high energy potential mikroflows, which appear in the final stage of slamming cavitation bubbles and affect the surface separation phase [4].

Sharp slamming of cavitation bubbles promotes the formation of water hammer, which leads to tension and compression waves in liquids with ultrasonic frequency. If the shock wave encounters an obstacle, it destroys or significantly distorts its surface [4].

Compatible cumulative effect of microflows and hydraulic hammers promotes sterilization and homogenization of processing foods, emulsification of liquids, grinding to micron-level the solid particulates and gas in the liquid, the intensification of chemical reactions in the dozens, and sometimes thousands of times [4].

In modern synchronous mixing saturation systems drinks saturation occurs in the flow through cavitation devices using artificial cavitation phenomena that is generated by hydrodynamic means by summing the gas component in the cavities of the main fluid flow. The biggest technological interest to intensify the process of carbonation the hydrodynamic cavitation devices with static cavitators have because they are one of the easiest and most effective ways to change the geometry of the current technological environment flow.

The maximum efficiency of the cavitation device depends on the design of static cavitator as much of the kinetic energy that occurs during the passage of environment flows through the device goes into the creation and continuous updating of the contact phases surface [3].

The most common construction for drinks saturation with carbon dioxide is the construction area of the cavitation device that operates on the Venture's principle and with overhead tank and pipelines is a major hub of carbonation unit (Fig. 1). The structure of the area of saturation is frame 1 pump mixing blending syrup prepared with water 2, pipelines 4, check valve 3, cavitation device 5, saturation pump 6, pressure regulator 7, pressure tank 9 with consumable socket 10 and a safety valve 8.

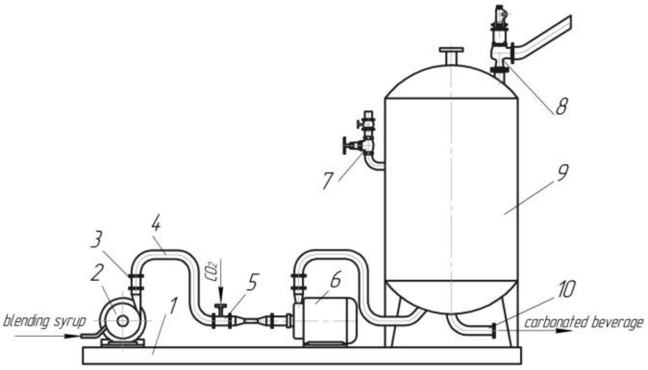

Fig. 1. Area of saturation with pressure tank

Venture Tube is a classic device for generating cavitation flow environment regime and constructively contains part, narrowing process flow, confuser, narrow neck with a critical section and the part that extends - diffuser. During the passage of fluid through a Venture tube, a critical crossroads neck the ring cavitation cavities forms, which increases with time, comes in a diffuser and splits to form a field of cavitation bubbles [3].

Area of saturation works in following way. Finished drink after mixing pump is fed to the saturation area. The flow rate of fluid is supported by a system of regulation in optimal range. Dilution, created at the site of cavitation device provides suction of carbon dioxide. The temporary increase of flow velocity promotes to distribution carbon dioxide in the stream and thereby provides quality mixing gas with the product.

Cavitation device that works on the principle of Venture has certain disadvantages. It does not provide phases contact enough for the saturation process liquid and gas, since it is the uneven distribution of carbon dioxide around all the intersection of fluid flow by introducing it only in the center of the flow and mixing drink with no carbon dioxide in the tube, which reduces the surface area contact of liquid and gas phases. The result is not very stable and strong bond two-phase system "drink-CO_2" and during decompression of drink not enough bound carbon dioxide is released from it. When you open the bottle cap you hear typical sound, indicating significant pressure undissolved CO_2 in the gas space of the bottle. "The Game" of bubbles in drinks is shorter and is occurred because of relatively large bubbles.

To correct these shortcomings the cavitation device to plot saturation were developed. It consists of housing 1, static cavitator 2 with the system internal channels 4 for supplying CO_2, blades on the outer surface cavitator 3 to tighten the flow of liquid and atomizers 5 for entry of carbon dioxide into the flow fluid (Fig. 2).

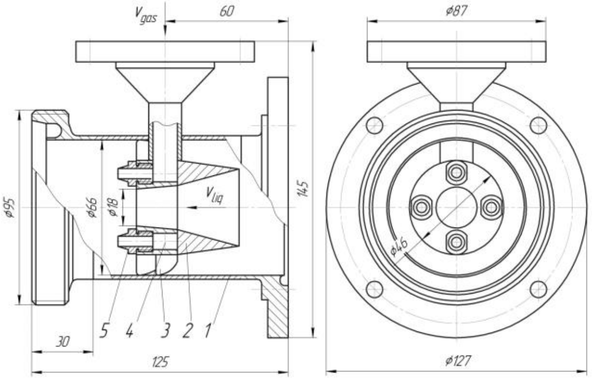

***Fig. 2.** Developed hydrodynamic cavitation device*

The overall flow of fluid passing through the cavitation device is divided into two streams: internal and external. The internal flow has a significant linear speed and injected carbon dioxide which is inserted into the cavity fluid flow appearing behind the cavitator. The external flow passing through the blade becomes large circumferential velocity, which promotes mixing of all liquid flow with gas behind the cavitator.

Experimental studies of existing and developed cavitation device was held in a production environment. Mineral water and fruit drinks were prepared and used as objects of study.

Effect of basic and additional factors on the process of drinks saturation and quality beverages saturation was investigated by synchronous mixing carbonation installation «Paramix» («KHS») in the area saturation of which in turn both cavitation device was set.

The efficiency of drink saturation, while working both cavitation devices, was defined in terms of loss of carbon dioxide during the technological cycle of drink production and also by organoleptic characteristics of drinks with full technological treating.

Five major and several additional factors have an significant influence the process of beverage saturation: 1) supply pressure of CO_2 into the drink; 2) the unit cost of CO_2 saturation; 3) the composition of the drink, 4) the temperature of the drink, 5) dilution is created in the previous aeration of water a) absorption coefficient; b) the specific surface area of updated contact phase; c) the duration of the contact phase [2].

During the research of the content of carbon dioxide in beverages only one parameter of various others was changing. It has been studied within the selected range, and other parameters maintained at a constant level. Value of carbon dioxide supply and its unit cost per saturation were at level of 0.5 MPa and 6.0 g/dm^3. Size of vacuum degasser in the degassing water was at 0.085 MPa pressure of CO_2 for additional degassing of water 0,2 MPa, the temperature of drinks 8 ° C.

To estimate the strength of a two-phase system "drink-CO_2" the measurements of residual carbon dioxide in mineral water, which was stored in open bottles under normal conditions, were carried out every day.

Dependence of CO_2 contents on temperature was determined for mineral water and fruit drink in the area of saturation with cavitation device of designed construction. An inverse relation is between temperature and degree of saturation drinks and mineral water. Graph of relation between mass concentration of CO_2 and temperature for mineral water (1) and drink (2) is shown in Fig. 3.

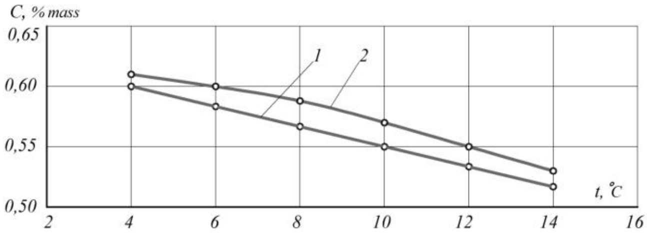

Fig. 3. *Graph of relation contents of CO_2 in beverages and their temperature.*

As a result, studies have found relation in which there is a decrease in mass concentration of carbon dioxide in mineral water and drinks with an increase in temperature.

Thus, the absorption ability of mineral water and drinks is as higher as the lower their temperature. That is why during the carbonation is recommended to seek a lower temperature to avoid extremely high pressures and saves carbon dioxide.

The dependence of the CO_2 mass concentration for mineral prepared water and fruit drinks from their component composition was determined for both cavitation devices ranging costs of carbon dioxide from 5.0 to 9.0 g/dm^3.

The best to be the saturation the fruit beverages, containing in its composition not only prepared water but sugar and a surface-active agents (flavors, dyes and ethanol). They reduce the surface tension of drinks, which provides to increasing the surface area of contact phases and facilitate better communication biphasic system "drink-CO_2." Mineral salts make worse this bond so mineral water is saturated with much worse than drink. Prepared water in the absence of mineral salts and surfactants saturated better than mineral water, but worse than fruit drinks [1, 5].

From the research results it follows that developed device promotes better absorption of liquid CO_2 and reduce loss of carbon dioxide to 10% with the same providing the saturation process conditions in comparison with the existing device.

The presence of air in the water and drinks during saturation has a negative impact on the degree of saturation by carbon dioxide. Beverages have a certain absorption capacity to the gas, so they each dissolved gas reduces the possibility of other dissolving gas [1, 2].

Research has shown that increasing the vacuum at degasser promotes the growth of CO_2 in beverages. Additional saturation of water with aeration also slightly increases the CO_2 in beverages.

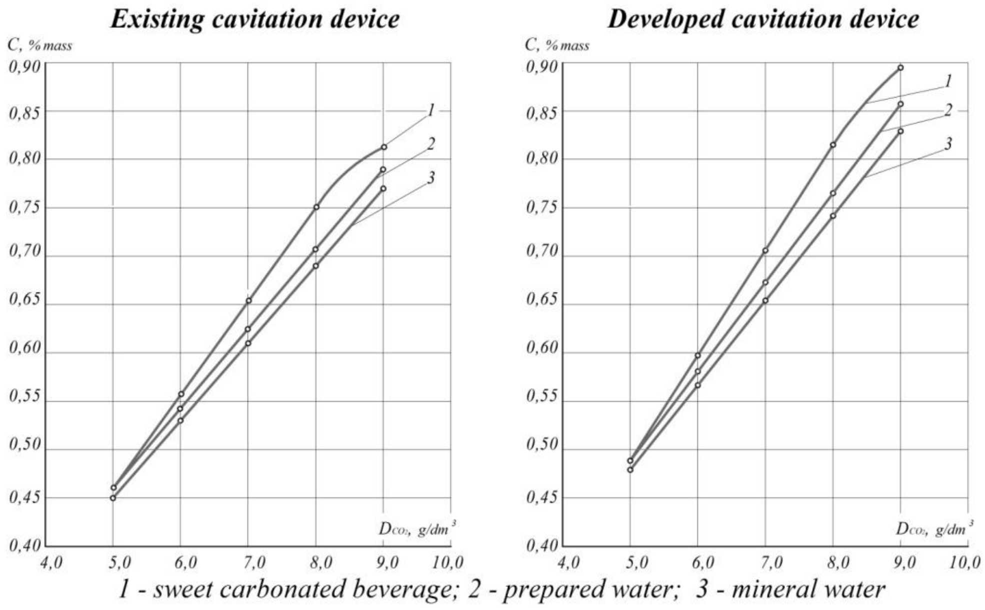

Fig.4. *Graph of relation between CO_2 contents in beverages and its cost to the saturation.*

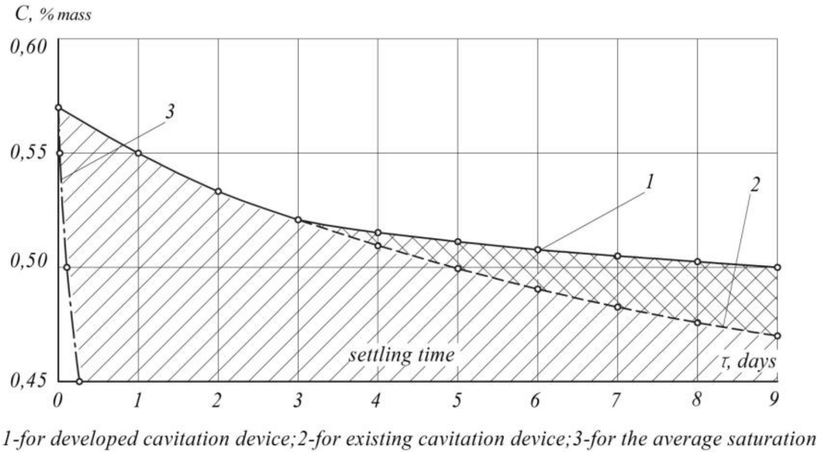

Fig. 5. *Graph of relation between CO_2 contents in the water and the duration of defending.*

To check the strength and quality of communication biphasic system "drink-CO_2" the research to determine the residual content of carbon dioxide in saturated mineral water was carried out. A number of bottles of aerated mineral water with an initial carbon dioxide content of 0.57 % of weight was selected for the experiment and was left to settle in bottles without caps at an ambient temperature of 25 ° C. The residual carbon dioxide in the water in these bottles was inspected every day. Measurement of residual CO_2 in water was carried out for 9 days.

As it can be seen from the graph (Fig. 5), even at the 9th day of settling the water contains 0.5 wt%. CO_2, which corresponds to the saturation of highly carbonated beverages. Saturation the mineral water by current device of CO_2 in water is kept slightly worse. For the average saturation time of a degassing drink takes only 2 to 14 hours.

The most influential factors on saturation are: unit cost of CO_2, vacuum during water degassing and temperature of the drink.

III. Conclusions

Thus, we can conclude the suitability of using cavitation devices with static cavitators within synchronous mixing constraction for carbonation of beverages in the flow. However, a characteristic feature of this type devices is a high technology reliability, the relative simplicity of construction, low specific energy consumption for processing the product. And, it is very important that they promote intensive and qualitative (homogeneous) mixing carbon dioxide with a drink, have a slight loss of CO_2. Due to thir help a high degree of saturation of drinks with carbon dioxide, increasing their biological stability is achieving and given level of physical and chemical parameters is supported.

The use of cavitation device designed structure in the carbonation setup allows increasing the contact surface liquid and gas phases, enhancing masstransfer, lowering specific energy costs and CO_2 losses, improving product quality.

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Contact:

Postgraduate Ruslan Petrikei. Department of machines and devices of food and pharmaceutical industries. National University of Food Technologies (Kyiv, Ukraine), petrikey@mail.ru.

MODELING OF CUTTING OF MULTILAYER MATERIALS

V. Goots, O. Gubenia, B. Lukianenko

National University of Food Technologies, Kyiv, Ukraine, e-mail: gubena@meta.ua

Abstract.

Introduction. *In the food industry products which have homogeneous or difficult multilayer structure are cut. Process of cutting for each case has many differences. It is necessary to fix features of movement of a knife in different products behind structure, and to improve regime parameters of operation of the cutting equipment.*

Materials and methods. *Mathematical simulation of movement of a knife in a product on the basis of the power assaying and the decision of differential second-kind equations is spent. For experimental researches installation of pendulum type with a knife that allows to change easily rate of a knife and a store of its kinetic energy is used.*

Results. *Mathematical sample pieces of cutting which allow to define force of cutting at different rates of a knife and product structure, and techniques of definition of factors, in mathematical sample pieces of cutting for different conditions of process are developed. If the product has a thin strong envelope, the force of cutting at knife approach to an envelope grows. It is reduced recommendations concerning conditions of movement of the cutting instrument, its orientation, concerning stratums to a product. At first it is necessary to cut a thin strong stratum, and then all volume of a product. It considerably reduces energy consumptions at cutting.*

Keywords: cutting, food, cutting regime, mathematical modeling, multi-layer, products.

I. Introduction.

In the food-processing industry machining job by cutting is applied to products which can be homogeneous for all volume (a sugar beet, the salted pork fat, meat without bones, confectionery masses but other), and for nonhomogeneous products which have an impregnation or an envelope. Structurally mechanical properties of an envelope differ from a product great bulk (fig. 1). For example, it is meat products which have interlayers from sinewy fabrics, a skin and bones; vegetables which have the strong outer heath; grain articles which consist of pulp and a strong rim. Stratums of these products are strong linked among themselves, and have different strength.

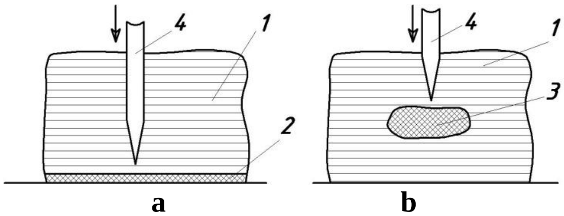

Fig. 1. Cutting of products with nonhomogeneous structure:

a - a product with an envelope; b - a product with an impregnation; 1 - a product, 2 - an envelope; 3 - an impregnation; 4 - a knife.

Analytical existing sample pieces of a cutoff have displayed that presence of impregnations or an envelope in a product it was not considered at simulation and optimisation of process of cutting.

Experimental researches prove [1- 4] that cutoffs of products with an envelope considerably differs from a cutoff of homogeneous products. At knife approach to an envelope there is a short-term increase in force of cutting, loads on a knife becomes pulsing, abrasion resistance of a knife decreases, quality of a surface of a cut is aggravated.

The envelope it can be on an input or an exit of a knife from a product, or to take place inside.

For definition of regularities of cutting of nonhomogeneous products on structure are spent analytical and experimental researches.

II. Materials and methods.

The technique of analytical probes assumes:

- The assaying of movement of a knife in a product under the influence of the affixed forces
- Working out of mathematical sample pieces of movement of a knife in a product on the basis of differential second-kind equations
- Definition of factors of mathematical sample pieces of a cutoff
- Practical recommendations about application of sample pieces for definition of force of cutting and a choice of rational parameters of process

The technique of experimental researches assumes use idle time on a construction, but with ample opportunities of application of the trial type. It is a floating lever [1, 3] (fig. 2) with a knife which at movement cuts a product.

Rate of a knife and its kinetic energy easily vary in considerable breaking points by balance start under a different edge and change of positions of a weight 3.

Rate of a knife it is defined on the basis of the differential equations of movement of a balance. The formula is as a result received:

$$V = R\sqrt{2\frac{\sum P_i r_i}{J}\left(1-\cos\beta\right)}$$

P_i - weight of each detail of a balance; R_i- distance from a detail barycentre to a shaft fulcrum pin; β - an edge of start or balance carriage, R - length of a balance; J - moment of inertia of all details of a balance.

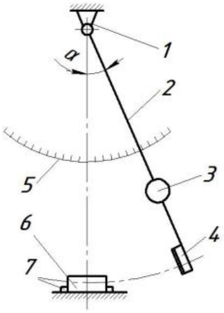

Fig. 2. The device for cutting process research:
1 - plate; 2 - balance; 3 - load; 4 - razor; 5 - scale; 6 - product; 7 - product fixator.

We define rate of an input and an exit of a knife from a product at various edges α balance start. The received experimental data we define forces of cutting and factors of mathematical sample pieces for various products on properties.

III. Result and discussing.

1. Simulation of a cutoff of homogeneous products

In case of product cutting, has homogeneous structure on all volume, on a knife forces operate:

- Cut F_r
- Friction (a dynamic friction)

$$G = C + k_1 V = C + k_1\frac{dy}{dt}$$

- Inertia

$$P_i = ma = \frac{m d^2 y(t)}{dt^2}$$

k_1 - the factors characterizing the friction; V, a - rate and knife speedup in a product.

Let's record the differential equation of movement of a knife:

$$F_r + G + P_i = 0 \Rightarrow \quad F_r + (C + k_1\frac{dy(t)}{dt}) + m\frac{d^2 y(t)}{dt^2} = 0 \qquad (1)$$

We solve the equations and it is spent some transformations. We receive the equation for definition of force of cutting depending on rate of a knife and properties of a product:

$$F_r = \frac{k_1\frac{dy(t)}{dt} - e^{-\frac{k_1\cdot t}{m}}(C + V_{oy}k_1) + C}{e^{-\frac{k_1\cdot t}{m}} - 1} \qquad (2)$$

The detailed assaying of the equation (2) and received results it is displayed in operation [3].

2. Simulation of a cutoff of nonhomogeneous products

Feature of a cutoff of nonhomogeneous products which have impregnations or an envelope, is short-term (instant) growth of force of cutting.

For such products of the equation of movement of a knife:

$$F_r + G + P_i + F_M = 0 \qquad (3)$$

Fm - instant forces.

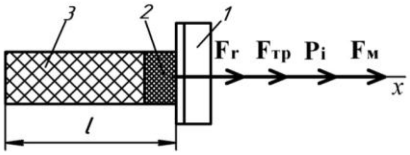

Fig. 3. *The forces operating on a knife:*
1 - a knife, 2 - an envelope, 3 - a product.

If impregnations is not on a product surface, and in its interior (fig. 1), the differential equation of movement of a knife looks like:

$$F_r + (c_1 x + \mu_1\frac{dy(t)}{dt}) + m\frac{d^2 y(t)}{dt^2} + F_M = 0 \qquad (1)$$

Where FM - quickly operating (instant) forces;

$$F_M = ke^{-(t-a)^n} \qquad (2)$$

k - the factor characterizing resistance of a cutoff of an impregnation. Its value depends on strength of an impregnation; a - the factor, defined impregnation arrangements in a product.

On fig. 4 influence of factors k and an on forces and an impregnation arrangement in a product is displayed.

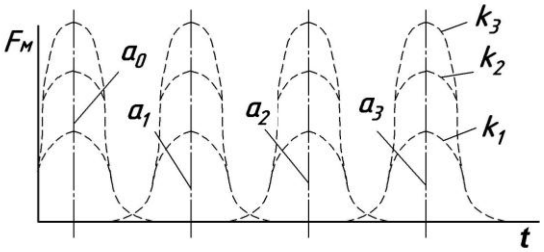

Fig. 4. *Impact of factors k and a on instant forces and an impregnation arrangement in a product; a3> a2> a1, k3> k2> k1*

The sizes of an impregnation are influenced by an apparent exponent n (fig. 5)

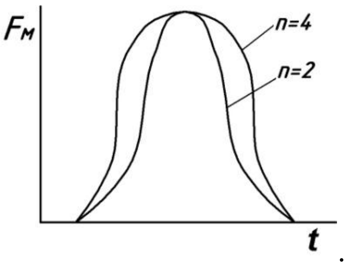

Fig. 5. *Influence of magnitude of an apparent exponent n on the sizes of an impregnation.*

Let's substitute F_M in the equation (1) and we will receive its decision. Under entry conditions t = 0 = x (0) = 0, V (0) = V0:

$$x(t)=\frac{m(F_p+c_1)(1-e^{-\frac{\mu_1 t}{m}})}{\mu_1^2}+\frac{1}{2}(2mV_0(1-e^{-\frac{\mu_1 t}{m}})+\sqrt{\pi}(erf(-t+a)-erf(a)+ \\ +e^{(-1/4\frac{\mu_1(-4am-\mu_1+4tm)}{m^2})}(erf(\frac{1}{2}\frac{\mu_1}{m}+a)-erf(-t+\frac{1}{2}\frac{\mu_1}{m}+a)))k-2t(F_p+c_1))/\mu_1 \tag{2}$$

$$V=\frac{(F_p+c_1)e^{-\frac{\mu_1 t}{m}}}{\mu_1}+(V_0\mu_1 e^{-\frac{\mu_1 t}{m}}+(-e^{-(-t+a)^2}-\frac{\sqrt{\pi}\mu_1 e^{(-\frac{\mu_1(-4am-\mu_1+4tm)}{4m^2})}(erf(\frac{1}{2}\frac{\mu_1}{m}+a)-erf(-t+\frac{1}{2}\frac{\mu_1}{m}+a))}{2m}+ \\ +e^{-\frac{\mu_1(-4am-\mu_1+4tm)}{4m^2}}e^{(-(-t+1/2\frac{\mu_1}{m}+a)^2)})k-F_p-c_1)/\mu_1 \tag{3}$$

From the equation (3) we define force of cutting:

$$F_p=\frac{1}{2}(2Vm\mu_1-2e^{-\frac{\mu_1 t}{m}}mc_1-2V_0\mu_1 e^{-\frac{\mu_1 t}{m}}m+2ke^{(-(-t+a)^2)}m+k\mu_1 e^{(\frac{\mu_1(4am+\mu_1-4tm)}{4m^2})}\sqrt{\pi}(erf(\frac{\mu_1+2am}{2m})- \\ -erf(\frac{-2tm+\mu_1+2am}{2m}))-2ke^{\frac{\mu_1(4am+\mu_1-4tm)-(-2tm+\mu_1+2am)^2}{4m^2}}m+2c_1m)/(m(e^{-\frac{\mu_1 t}{m}}-1)) \tag{4}$$

The received equations are difficult for the analytical assaying, at execution of practical calculations and use of computer methods of character mathematics demand.

Let's consider possibilities of simplification of definition of force F_M.

If on a product surface the stratum is placed (an envelope, a rim, a packing film), the instant force can vary under such laws:

$$F_M=Be^{-bt} \tag{5}$$

or

$$F_M=Ae^{-B(\ln t)^2} \tag{6}$$

Change of instant force on time is displayed on fig. 6. Graphically it is figured as quickly falling down dependence. Time of its operation 0 - t1 is much less, than duration of movement of a knife in a product.

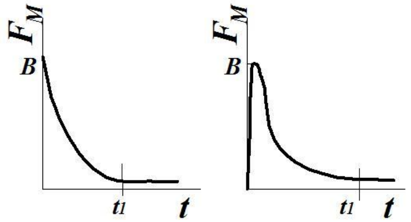

Fig. 6. *Change of instant force on time.*

At the differential equation of movement of a knife:

$$F_r + (C + k_1 \frac{dy(t)}{dt}) + m\frac{d^2 y(t)}{dt^2} + Be^{-bt} = 0 \qquad (7)$$

We solve the equations under entry conditions t = 0 = x (0) = 0, V (0) = V0 we receive a value of migration (8), rates of a knife (9) in a product and force of cutting (10).

$$y(t) = \frac{m(1-e^{-\frac{\mu_1 t}{m}})\left(V_0\mu_1 + C_{\text{тр}} + F_p\right)}{\mu_1^2} + \frac{\mu_1\left(B\left(1-e^{(bt)}\right) + bt\left(C_{\text{тр}} + F_p\right)\right) - mb(bt\left(C_{\text{тр}} + F_p\right) + B(1-e^{-\frac{\mu_1 t}{m}}))}{(mb-\mu_1)\mu_1 b} \qquad (8)$$

$$V(t) = \frac{e^{-\frac{\mu_1 t}{m}}\left(V_0\mu_1 + C_{\text{тр}} + F_p\right)}{\mu_1} + \frac{\mu_1\left(Bbe^{(-bt)} + b\left(C_{\text{тр}} + F_p\right)\right) - mb(b(C_{\text{тр}} + F_p) + \frac{B\mu_1 e^{-\frac{\mu_1 t}{m}}}{m})}{(mb-\mu_1)\mu_1 b} \qquad (9)$$

$$F_p = \frac{V\mu_1 mb - V\mu_1^2 - e^{-\frac{\mu_1 t}{m}}V_0\mu_1 mb + e^{-\frac{\mu_1 t}{m}}V_0\mu_1^2 - e^{-\frac{\mu_1 t}{m}}mbC_{\text{тр}} + e^{-\frac{\mu_1 t}{m}}\mu_1 C_{\text{тр}} - \mu_1 Be^{(-bt)} - \mu_1 C_{\text{тр}} + C_{\text{тр}}bm + B\mu_1 e^{-\frac{\mu_1 t}{m}}}{e^{-\frac{\mu_1 t}{m}}mb - e^{-\frac{\mu_1 t}{m}}\mu_1 + \mu_1 - mb} \qquad (10)$$

On fig. 7 change of instant force depending on factor is displayed in which strength and structurally-mechanical properties of an envelope influence.

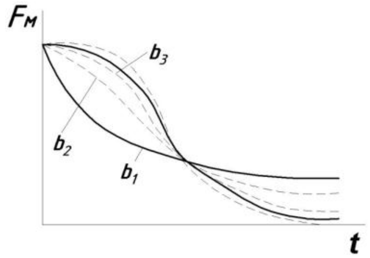

Fig. 7. *Dependence of instant force F_M of an apparent exponent of B*

We define power of cutting as product of force of cutting for rate of a knife.

$$N = F_{rm}\frac{dy(t)}{dt}$$

F_{rm} - the maximum force of cutting.

If instant force, $F_M = Ae^{-B(\ln t)^2}$ the equation of movement of a knife:

$$F_r + (C + k_1 \frac{dy(t)}{dt}) + m\frac{d^2 y(t)}{dt^2} + Ae^{-B(\ln t)^2} = 0 \qquad (11)$$

We solve the equations under the same entry conditions, we recognize forces of cutting:

$$F_r = \frac{\mu_1(V - e^{-\frac{\mu_1 t}{m}}V_0) - e^{-\frac{\mu_1 t}{m}}C + A\int_0^t \frac{\mu_1 e^{-\frac{b\ln U^2 m - \mu_1 t + \mu_1 U}{m}}}{m}dU - Ae^{b\ln(t)^2} + A\left(\frac{\partial}{\partial t}invlaplace\left(\frac{laplace\left(e^{b\ln(t)^2}, t, s_1\right)}{s_1}, t, s_1\right)\right) + C}{e^{\left(-\frac{\mu_1 t}{m}\right)} - 1} \qquad (12)$$

The equation powers up special functions, therefore it is expedient to execute its decision the approximate methods in the form of a polynomial or numerical methods.

Change of force of cutting in the presence of an envelope it is confirmed experimentally. It is received forces of a cutoff of meat with a sinewy interlayer according to the equation (2). An interlayer took place on an input or an exit of a knife from a product. The force of cutting separately sinewy laminations small, also was not fixed by gears. But forces of a cutoff of meat increases at stratum arranging on an exit of a knife from a product (fig. 8).

Adequacy of the received sample pieces is confirmed for not foodstuff. For example, presence of a thin polymeric film on a cardboard augments forces of its cutoff at 20-50 time under condition of film arranging on a knife exit.

On the basis of the spent probes following outputs and recommendations are drawn:

The product structure influences force of cutting. Presence of an envelope and its arranging on an exit of a knife from a product (fig. 9a) considerably augments force of cutting, therefore so to cut a product of the irrational

At a cutoff the envelope should take place on a knife input in a product, or is perpendicular to a knife (fig. 9,). At execution of this condition the force of cutting decreases, quality of a cut and a period of operation of the cutting instrument raises.

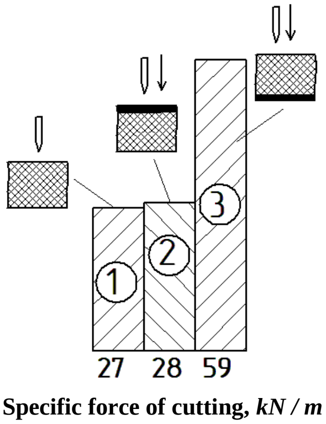

Fig. 8. *Dependence of force of cutting of meat on arranging sinewy a stratum:*
1 - without an interlayer, 2 - a stratum on a knife input in a product, 3 - a stratum on an exit of a knife from a product.

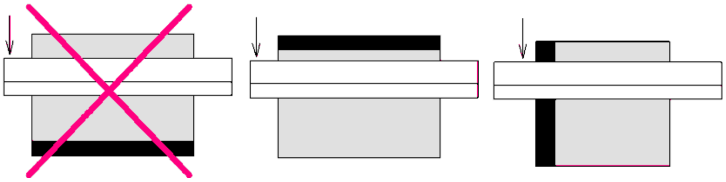

Fig. 9. *Arranging of an envelope concerning knife movement.*

IV. Conclusions

Process of a cutoff of products, homogeneous or have an envelope or an impregnation, considerably differs.

At knife approach to an envelope of force of cutting it is augmented multiply under the exponential law.

Mathematical sample pieces of movement of a knife are developed allow to define force of cutting for various products on structure.

At a cutoff of multilayer products at first it is necessary to cut a thin strong stratum. It allows to lower expenditures of energy for cutting process.

Results can be applied at a choice of conditions and conditions of cutting of foodstuff and many other materials, in particular, the packing.

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OPPORTUNITIES FOR WASTE MATERIALS UTILIZATION BY EXTRUSION IN PROCESSING COCOA SEEDS

I. N. Panchev, N. G. Toshkov, V. B. Nenov, A. T. Simitchiev

University of Food Technology, Plovdiv 4002, 26 Maritsa Blvd., tel.: 032/60 37 15,
e-mail: ivan_n_panchev@abv.bg

Abstract: *This paper examines the use of extrusion in processing cocoa shells - waste products in chocolate production. It was found that the extrudates obtained in the form of stripes and the mixtures of cornmeal with 4% cocoa shells obtained in the form of sticks, possess good organoleptic properties and water sorption capacity, which allows us to recommend extrusion processing of cocoa shells as an alternative technology in waste-free processing of raw cocoa materials.*

Keywords: extrusion, extruder parameters, modeling, sorption.

I. Introduction

Cocoa seeds called "food of the gods" are key raw materials in a number of food, cosmetic and pharmaceutical technologies. During their pre-treatment, after they are baked and grinded, they are separated as waste material shells (cocoa shells), which contain valuable biologically active substances such as polysaccharides, proteins, vitamins, caffeine, tannin, organic acids, etc. The issue regarding the rational use of cocoa shells has been long investigated, but no satisfactory decision has been found so far [1, 6]. Shells are known to be used as animal feed, for making fuel briquettes, for fertilizing and improving the soil, for heavy metal sorption in wastewater, for producing alcohol, furfural, theobromine, for making thermoset resins, acoustic and thermal insulation panels, paper, as pasta ingredients, to prevent deposit formation in pipelines, etc. [4, 8, 10, 11, 12, 14]. Despite the large number of technologies available and used for processing cocoa shells, none has received widespread application, hence the necessity to continue studies on the utilization of these waste products towards waste-free chocolate production.

The aim of this work is to explore the potential use of cocoa shells in food extrusion.

II. Materials and methods

Cocoa shells from seeds of cocoa of the "Rio" cultivar were used - waste materials in the production of chocolate kindly provided to us by the "Gayo Chocolate" company from Plovdiv. The shells separated after roasting and grinding of the cocoa seeds were analyzed for chemical composition and dispersion using standard methods. The water binding capacity of the shells and of the extruded products were tested by the classical gravimetric method, and their structure was visualized using scanning electron microscopy (SEM) with Jeol CEM T-200, Japan.

Taking the sorption isotherms of the investigated cocoa shells and of the extrudates was done using the classic static gravimetric method recommended for food products [3]. Samples with an initial mass of 1 ± 0,05 g were weighed in weighing vessels. The containers were placed in hygrostats over saturated salt solutions of eight salts (LiCL, MgCL2, K2CO3, Mg(NO3)2, NaBr, NaCL, KBr, KCL) maintaining water activity of the product in the range of 0,11 to 0,85 [9]. The hygrostats were heated in a thermostat at 25 ± 0,1 °C. After reaching equilibrium (day 20 to day 30), the moisture of the samples was evaluated by the weighing method (24h at 105 °C). All experiments were performed in three repetitions. The sorption isotherms were described using the two-parameter models of Chung-Pfost, Halsey, Oswin, Henderson, as recommended in [2,7]:

Chung-Pfost $$\ln(a_w) = -A\exp(-BM), \quad (1)$$

Halsey $$a_w = -\exp(AM^B), \quad (2)$$

Oswin $$M = B\left[\left(\frac{a_w}{1-a_w}\right)\right]^C, \quad (3)$$

Henderson $$\ln(1-a_w) = -AM^B, \quad (4)$$

where: M stands for the equilibrium moisture content, % dry mass; a_w - water activity; A, B, C – constants.

To determine the monomolecular moisture, we used the well-known model of Brunauer-Emmett-Teler (BET) [13] valid for $a_w < 0,5$ [3]:

BET $$M = \frac{M_m C a_w}{(1-a_w)(1-a_w+Ca_w)}, \quad (5)$$

where: M_m designates monomolecular moisture, % cm; C - constant.

Extrusion of cocoa shells and of the semolina and cornmeal mixed with them was implemented with extruder "Brabender 20DN", Germany, equipped with a screw with a compression ratio 4:1, nozzle diameter D_d=2,5 mm, in operating modes: temperature of Zone I t_1 =150^0 C, temperature of Zone II t_2 =155 ^{0}C, temperature of Zone III t_3 =160 ^{0}C, dosing screw rpm N_1 = 40 min^{-1}, working screw rpm N_2. = 200 min^{-1}, screw torque M = 46 Nm, pressure P = 6,4 MPa, mold temperature tm = 170 ^{0}C. The concentration of cocoa shells in mixtures with semolina and cornmeal was 4%.

III. Results and discussion

Experimentally obtained sorption isotherms of the cocoa shells, of the extruded stripes thereof and of the cylindrical extrudates from cocoa shells and cornmeal are presented in Figure 1. This figure shows that the isotherms have a typical S-shape, i.e. they are of type II according to Brunauer's classification [3]. Experimental data show that extruded stripes have the highest sorption capacity, while cylindrical extrudates have the lowest sorption capacity, as this trend is more pronounced at the higher water activity levels (aw > 0,6). It is typical of cocoa shells that they manifest the lowest sorption capacity for water activity up to 0,5, after which their sorption capacity rises and virtually equals that of stripes extruded from them

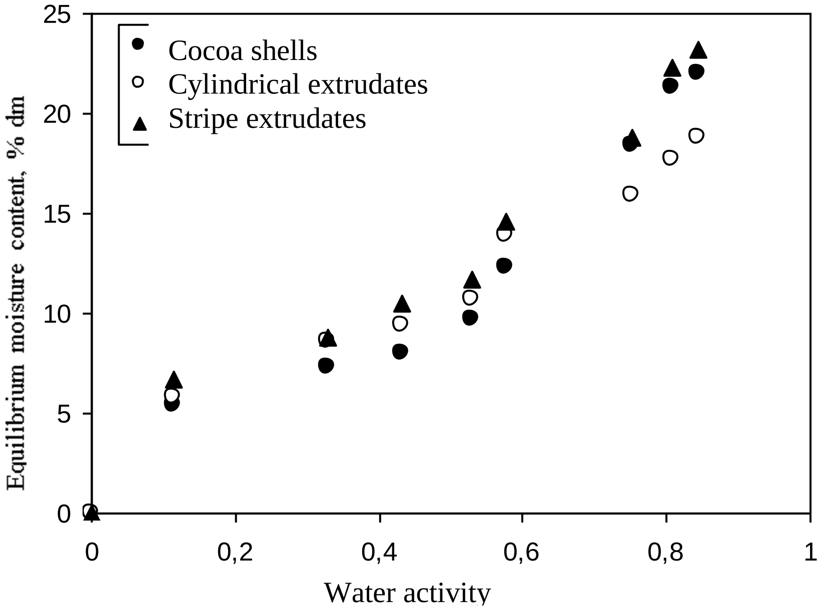

Figure 1. *Equilibrium isotherms for cocoa shells, cylindrical extrudates and stripe extrudates*

The coefficients of the linear equations were determined by the least squares method. The coefficients, the average relative error P and the standard deviation SD of models (1) to (4), for cocoa shells, cylindrical extrudates, and stripe extrudates, are shown in Tables 1, 2 and 3, respectively. For samples of cocoa shells and stripe extrudates, the lowest values of the average relative error and the standard deviation were obtained for the model of Halsey, while for the cylindrical extrudates they were obtained for the model of Oswin. The differences in the P and SD values for the model of Oswin and for the model of Halsey for the cylindrical extrudates were negligible, so the model of Halsey can be recommended to describe the sorption isotherms of the three products tested.

Table 1. *Model coefficients (A,B), average relative error (P,%) and standard deviation (SEM) for cocoa shells*

Model	*A*	*B*	*P*	*SEM*
Chung-Pfost	2,868	0,1279	14,27	1,76
Oswin	0,4169	10,64297	9,97	1,39
Halsey	28,769	-1,6226	6,66	1,06
Henderson	0,0142	1,6022	13,69	1,72

Table 2. *Model coefficients (A,B), average relative error (P,%) and standard deviation (SEM) for cylindrical extrudates*

Model	*A*	*B*	*P*	*SEM*
Chung-Pfost	5,504	0,184	5,61	0,86
Oswin	0,323	11,041	4,17	0,84
Halsey	97,69	-2,106	5,05	1,17
Henderson	0,0034	2,17	6,77	0,96

Table 3. *Model coefficients (A,B), average relative error (P,%) and standard deviation (SD) for stripe extrudates*

Model	*A*	*B*	*P*	*SD*
Chung-Pfost	4,019	0,1373	8,85	1,3
Oswin	0,355	12,493	6,74	1,04
Halsey	81,581	-1,9315	3,89	0,81
Henderson	0,0048	1,9312	9,53	1,5

To calculate the monomolecular moisture content, equation (5) can be transformed into a linear form:

$$\frac{a_w}{M(1-a_w)} = \frac{1}{MmC} + \frac{(1-C)a_w}{MmC}. \qquad (6)$$

Based on the slope, using the least squares method, the coefficients of linear equation (6), and hence the monomolecular moisture content and coefficient C can be determined. The linear dependence $a_w/[M(1-a_w)] = f(a_w)$, with experimental data on the extruded stripes at $a_w < 0,5$ is shown on Figure 2. The dependences for the other two products were derived in the same way and are therefore not shown here. The obtained monomolecular moisture values and the correlation coefficients for the three products under study are presented in Table 4.

Table 4. *Monomolecular moisture (* M_m *) and correlation coefficients (* R^2 *)*

Product	M_m	R^2
Cocoa shells	4,57	0,994
Cylindrical extrudates	5,49	0,99
Stripe extrudates	5,97	0,99

The results show that the monomolecular moisture content in the extruded stripes was 23,5% higher than that in cocoa shells and only 8% higher in comparison to that in cylindrical extrudates. It can be concluded that extruded products have higher monomolecular moisture and can be stored at high water activity, respectively, at higher relative humidity of the air.

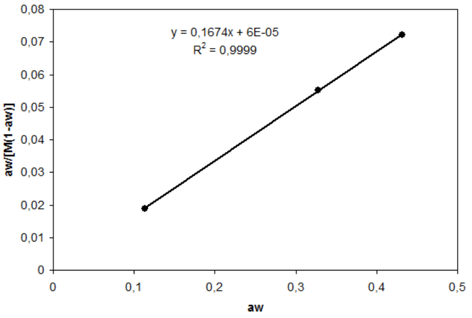

Figure 2. *Dependence for extruded trips*

Structural studies carried out using SEM reveal in Fig. 3 a, b, c, d, that extruded cocoa shells and their mixtures with cornmeal have a sophisticated capillary-porous structure responsible for their high water sorption capacity. Organoleptic evaluations showed that the sticks extruded from cocoa shells and their mixtures with semolina are very hard and unacceptable for a normal chewing process, while in the form of extruded stripes or sticks mixed with cornmeal, they have normal mechanical properties and the typical flavor of roasted cocoa, which makes them spicy foods. The specific chocolate flavor intrinsic to the extrusion of cocoa shells is definitely an advantage in a similar approach for other raw materials, which have to be flavored after extrusion due to loss of aromatic substances caused by high temperature and pressure used in the extrusion process [5].

IV. Conclusions

The results show that cocoa husks can be mixed with wheat and corn meal to produce expanded products by hot extrusion. Found that the extrudates obtained in the form of stripes and the mixtures of cornmeal with 4% cocoa shells obtained in the form of sticks, possess good organoleptic properties and water sorption capacity. Sorption isotherms obtained are of type II according to the classification of Brunauer and their description suitable model Halsey. Monolayer capacity in the range 4,57 ÷ 5,97% s.m.

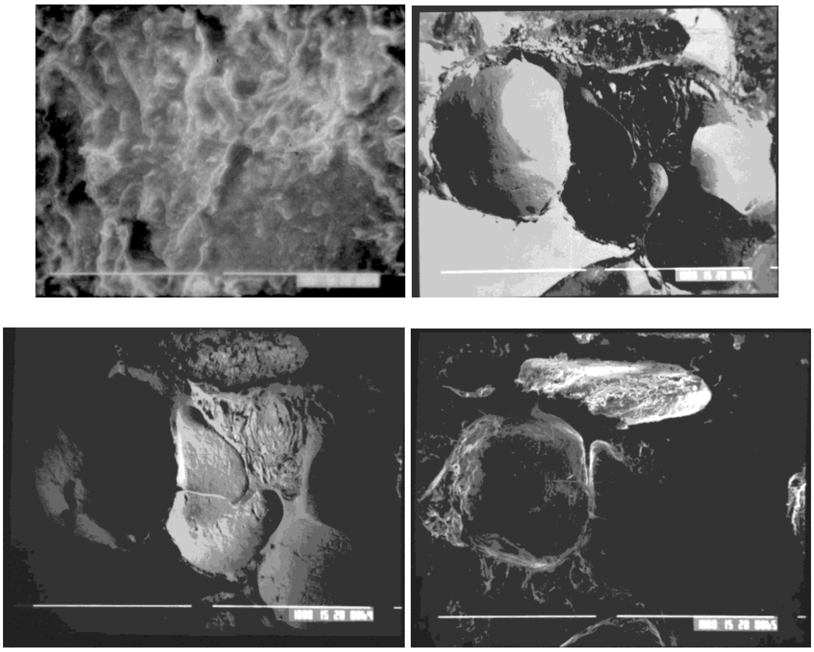

Figure 3. *SEM of extruded samples containing cocoa shells*

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DETERMINING THE AGGREGATE OBJECTIVE FUNCTION IN A STUDY OF THE PROCESS OF COFFEE TABLETING

I. N. Shopov

Associate Professor, Dr., engineer, department 'Mechanical Instrument Engineering', Technical University Sofia - branch Plovdiv, Plovdiv, 25 Tsanko Dustabanov str., tel. 0885537762, e-mail: ivan_chopov@abv.bg

Abstract: *One of the advantages of a tableting is the opportunity for absolutely accurate dosing of the different varieties of coffee in the volume of a tablet. This article has been tasked to determine the aggregate objective function with which to assess the complex effects of substances contained in coffee on the human body. The construction of a summary function is demonstrated, evaluating opportunities to improve the mental stability and prevent cancer, using the function of desirability of Harrington.*

Keywords: study, coffee tableting

I. Introduction

The coffee preparation for consumption is a result of multiple processes, each of which affects the composition and flavor characteristics of the coffee beverage: storage, mixing of the various species, sintering, grinding, tableting or encapsulating, packaging with or without the presence of air, extraction. One of the advantages of tableting is the opportunity for absolutely accurate dosing of the different varieties of coffee in the volume of a tablet.

Studies of the influence of tableting on the final product are preceded by a stage called pre-planning the experiment. An important part of pre-planning the experiment is defining the objective function. Data from various studies show that the green coffee contains more than 2,000 substances. Each of these substances affects somehow the human body both separately and synergistically. Therefore, the possibilities for the formulation of an objective function are a huge number and there is danger while achieving the desired result in terms of a substance another important matter to be excluded from monitoring. The only way to avoid this drawback of the study is to formulate an aggregate (complex) objective function that will combine in itself the beneficial effects of several studied input factors / substances /.

The goal of this publication is to show the way to formulate a complex objective function with the above-described features in a study process of the coffee tableting.

1. *Content of substances in coffee*

- ***water***

The degree of humidity of the raw coffee is essential for the assessment of its quality. The moisture content of raw coffee plays an important role in the export or import as all payments between suppliers and buyers of coffee are made on the basis of the indicator for humidity, expressed as a percentage. (1)

Raw coffee beans are related to the product group having capillary - porous colloidal structure. These are specific for different forms of the connection of water with the material (free, connected, firmly connected). The water content of raw coffee beans by the standards of the International Coffee Organization should be 12 ± 1%. However, depending on the conditions of storage and transport, the humidity of unroasted coffee varies in the range from 9 to 14%.

At relative humidity of 40-60%, the moisture content in the grains does not exceed 12%. At humidity of 63-65%, raw coffee saves its natural color, freshness and taste for a year; at humidity of 65-70%, except the yellow coloration a characteristic smell and taste of unsold coffee appears.

- ***substances to be extracted***

The content of water-soluble extractive substances in various types and varieties of green coffee is not the same and is, for example, 20 - 29%. The smallest amount is in Arabica (19-20%).

In the composition of the extracted substances of the raw coffee are alkaloids, proteins, phenolic compounds, mono-and disaccharides, lipids, organic acids, amino acids, mineral elements and a number of other substances presented in a small amount.

- ***caffeine***

Caffeine ($C_8H_{10}N_4O_2$) - is the most important alkaloid in coffee beans (fig. 1). This substance is colorless and odorless, which in single solution gives a bitter flavor. Water solutions of caffeine are neutral, and with acids caffeine forms salts. Caffeine in raw coffee is both free and in relation to compounds of potassium status. Different types of coffee are characterized by the following state of caffeine: Arabica - 0.6 to 1.2, Robusta - 1.8 to 3, Liberica - 1,2 to 1,5 (% of dry matter). The amount of caffeine in the beans, plays a very important role in assessing the quality of raw materials and establishing technical requirements for it.

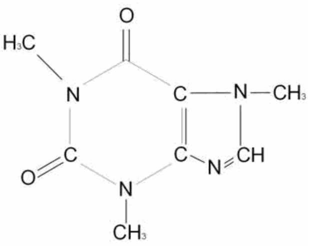


Fig. 1 *Structural formula of caffeine*

- ***trigonelline***

Trigonelline ($C_7H_7O_2N$), or metilbetainikotinova acid in plants is formed by the methylation of the nicotinic acid. This alkaloid is contained in a large amount in varieties of coffee of Arabica (1-1.2%). In Robusta, it is less (from 0.6 to 0.74%), and in the types of Liberica - only 0.2-0.3%. Trigonelline dissolves in water but is thermally unstable. When processing of the coffee beans it can be easily converted into nicotinic acid (vitamin PP), therefore it is considered to be a major precursor for the formation of nicotinic acid in the coffee beans.

- ***theobromine***

Theobromine is dimethylxanthine ($C_7H_8O_2N_4$), as by oxidation monomethyl alloxan and monomethyl urea are formed. It is a colorless powder with small crystals, hard to be dissolved in water. Theobromine is melted at 351° C , capable to evaporate, dissolved in slightly active bases from which sodium salt is prepared. The content of theobromine in raw coffee beans is negligible - 1.5-2.5 % mg.

- ***theophylline***

Theophylline is 1,3 - dimethylxanthine ($C_7H_8O_2N_4$), which forms colorless needles containing one molecule of water of crystallization. Theophylline is hard to be dissolved in cold water, melts at 269-272 º C. Total amount of grains in the wild coffee plant is 1-4 % mg.

- ***chlorogenic acids***

Chlorogenic acids constitute the bulk of the phenolic compounds. They are mono and di-esters of β-phenyl acrylic acid and quinic acid. Raw coffee beans contain 7-10% chlorogenic acids. During the roasting of the coffee the content of these acids decreases sharply - about 65 - 67%.

- ***tannin***

In raw coffee beans tannin content varies widely - from 3.6 to 7.7%. In the roasting process of the coffee (especially at a temperature of 175-205 ° C) the amount of tannin sharply decreases and in the ready product it remains 0.5-1.0%. This is one of the labile components of the coffee, which is oxidized vigorously during 5-8 minutes of heat treatment at a temperature of 80-125 ° C.

- ***Hydrocarbons***

Hydrocarbons constitute 50-60% of the total weight of the coffee beans. The composition of the hydrocarbons includes sucrose (6-10%), cellulose (5-12%), pectin substances (2-3%) and high molecular weight polysaccharides (fibers, lignin, etc.). It has been thought for a long time that the raw coffee does not contain free mono-saccharides (glucose and fructose), but studies have found out that in the coffee beans of Arabica sucrose predominates, while in Robusta type - reducing sugars. Generally the total amount of reducing sugars in coffee beans reaches 0.7 - 1%.

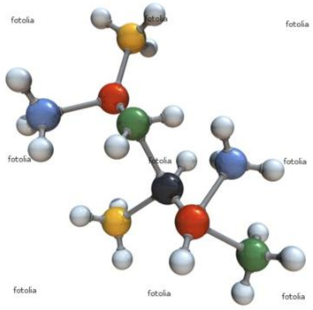


Fig. 2 *Visualization of the structure of the hydrocarbons*

- ***proteins***

In raw coffee of the three main varieties (Arabica, Robusta and Liberica) protein is in almost the same amount - the total protein content is from 9.69 to 10.19%.

- ***Lipids***

Coffee oil has a liquid consistency and contains glycerides of palmitic, stearic, linoleic and caprylic acids. Fatty substances remain almost completely in the dry phase and do not pass in the prepared drink.

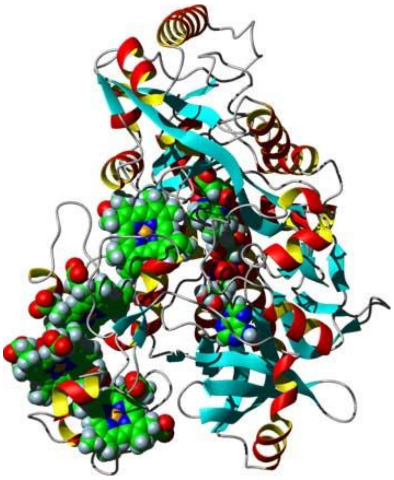


Fig.3 *Visualization of the structure of proteins and lipids*

- ***organic acids and minerals***

In the raw coffee beans there are citric acid, malic acid, maleic acid, acetic acid and a dibasic carboxylic acid. The acidity of raw coffee of different botanical varieties and vary from 2.4 to 4 ° T.

In raw coffee beans, mineral content constitutes 3-4,5%. The predominant component is potassium - about half, followed by the magnesium and calcium (around 10-fold less), sodium, iron, manganese. It is considered that the high content of zinc, manganese and rubidium contributes to improving the properties of the coffee. During coffee roasting, mineral content is increased to 5-7%, which is connected with a great loss of dry matter.

Content of substances in coffee is described according to data from (1).

3. Opportunities and goals in the choice of objective function

The choice of the objective function in the study of the ready brewed product should be made primarily taking into consideration the influence of coffee on the human body. Moreover, we can distinguish four main ways of influence of coffee beverage on the body: **an uplifting effect, long-term benefits for human health, harmful effect, taste**. It should always be had in mind that thousands of studies have been conducted on the impact of coffee on people, some of them have contradictory conclusions and myths have been created.

- Undoubtedly there is a benefit of coffee as a means of improving mental and physical performance. The benefits of coffee are demonstrated to enhance the cogitative abilities. However, this only applies to those who are engaged in logical thinking.

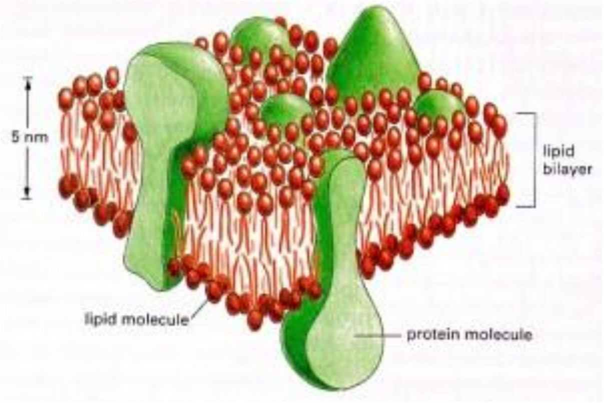


Fig.4 *Function of desirability*

The benefit of coffee for mental health is expressed also in increasing the resistance to stress. It reduces the risk of falling into depression and suicide as the risk decreases with increasing the amount of coffee consumed. (2)

Since this effect is clearly associated with caffeine, clearly the presence of caffeine in the beverage will be assigned as one of the possible functions of the study. Caffeine is also used in the treatment of diseases of the central nervous system.

- It is believed that only two cups of coffee per day lower the possibility of occurrence of cancer of the liver, pancreas, colon and rectum. As for smokers, coffee reduces the risks of cancer in the blood. These effects are achieved, according to some Canadian scientists, at the expense of the substance of trigonelline, and according to others at the expense of the general content of antioxidant substances. Therefore, the content of antioxidants and trigonelline may be a objective function in the study.

- There is evidence that coffee improves sexual function in men by increasing the physical activity of the sperm. The possibilities for sports activities improve, increasing the endurance.

Other researchers argue that coffee has a favorable effect on digestion. In both mentioned effects, however, the impact of the coffee is not a function of the presence of a specific substance in the beverage. Therefore, they can hardly define an objective function.

- In the process of long-term study of coffee some persistent myths are debunked. For example, it has been shown that coffee does not cause coronary heart disease; it does not cause cancer; it does not induce malformations of the fetus during pregnancy as well as many other diseases.

Harmful effects of coffee consist of short-term rises in blood pressure, diuretic effects for people having kidney diseases, premature termination of pregnancy, "washing" of some micronutrients from the body, causing dependency (3). These effects are related to the excessive use of coffee during the day, for example, 6 or more cups per day, the most important and the strongest effect is the first cup. In this sense, when determining the objective function such considerations could lead to determination of an upper limit of the elements contained in one dose of coffee at a fixed upper limit on the number of cups per day.

In any case, it should be had in mind that the effect of coffee is an individual, especially in terms of taste. So everyone has to choose their optimal dose alone, and of course to make an informed choice by researchers.

II. Methods for selecting the objective function

The correct choice of the objective function determines the significance of the study for practice and ensures successful resolution of the problem. The objective function depends largely on the type of mathematical model, and thus the opportunities for optimization.

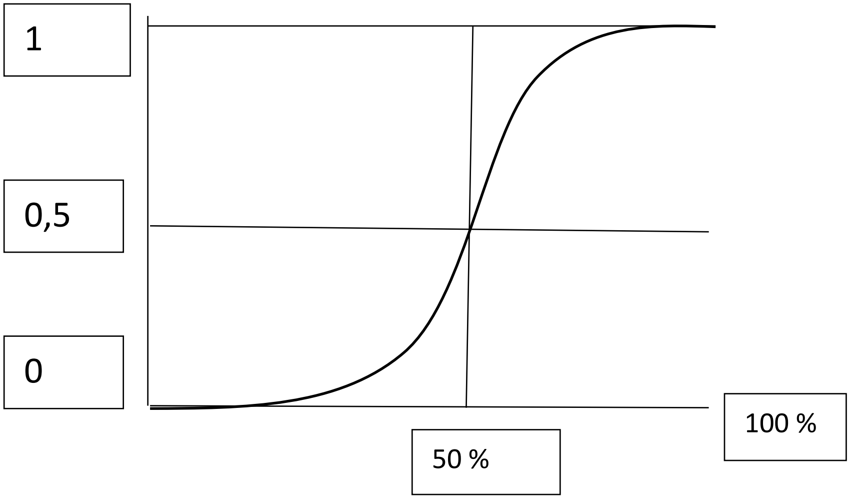
Objective function must be quantified with a clear physical meaning. It must have the ability universality as thoroughly and completely characterizes the purpose of the study.

It is necessary the objective function to be statistically efficient, i.e. to be determined with the greatest accuracy. To be an effective test, it must be unique, so the number of parameters of the optimization has to be reduced. Effective ways to reduce the number of parameters of the optimization are (4):

- **obtaining summary parameter of optimization** (aggregated objective function)
- the method of priori ranking
- method of correlation analysis
- segmenting the complex task with large number of objective functions into several simple ones, with accurately defined parameter of optimization and their consistent solution

Due to the presence of multiple substances (according to some experts more than 2,000 substances in the green coffee) in the composition of the coffee and the inevitable presence of the whole bunch of ingredients in the starting material which act individually as well as synergistically, it can be assumed that the use of aggregated objective function is the most suitable method for studying the process of brewing and its impact on the quality of the final product. This approach, however, may be hindered by the complexity and appreciation of experimental methods and tools for conducting the study. In this case, the segmenting of the complex task into a number of more simple ones and accessible to study objective functions and their consistent solution will be effective in achieving a relevant result.

One of the most convenient methods for obtaining summary response / summary / objective function is a generalized function of desirability of Harrington. The scale of desirability refers to psycho physical scales. The basis of the construction of this generalized function is the idea to convert the natural values of private responses to a dimensionless desirability scale of Fig. 4.



To obtain the scale it is convenient to be used the standard already developed correlation tables of correspondence between preferences in empirical form and numerical psychological one.

The value of the private response, converted into a dimensionless desirability scale is denoted by d_u, where u = 1,2,3 ... n and is called private desirability. The transition from private to a summary desirability function is performed by the formula (5):

Table 1. *Standard values of the scale of desirability*

Desirability	Values
Very well	1 – 0,80
Well	0,80 – 0,63
Satisfactorily	0,63 – 0,37
Poorly	0,37 – 0,20
Very poorly	0,20 - 0

$$D = \sqrt[n]{\prod_{u=1}^{n} d_u} \qquad (1)$$

Where, D is an aggregate desirability function; d_u are private desirabilities.

Let us form a generalized objective function for a coffee beverage, which can explore the possibility of simultaneously invigorating, improving mental and physical strength and at the same time the human body to be prevented from various types of cancer. For this purpose, trigonelline and caffeine should fluctuate within the following limits:

Trigonelline: 0.6 to 0.74% of dry matter

Caffeine: 1.8 to 3% of dry matter

Tabular conversion to private functions of desirability is shown in Table 2 and Table. 3. After completion of the experiment, the transition to a summary function is by formula (1).

Table 2. *Private function desirability of trigonelline*

Desirability	Values of the content of trigonelline in% of dry matter	
Very well	1 – 0,80	0,74 – 0,712
Well	0,80 – 0,63	0,712 – 0,6882
Satisfactorily	0,63 – 0,37	0,682 – 0,65518
Poorly	0,37 – 0,20	0,65518 – 0,628
Very poorly	0,20 - 0	0,628 - 0

Table 3. *Private function desirability of caffein*

Desirability	Values of the content of caffeine in% of dry matter	
Very well	1 – 0,80	3 – 2,76
Well	0,80 – 0,63	2,76 – 2,556
Satisfactorily	0,63 – 0,37	2,556 – 2,244
Poorly	0,37 – 0,20	2,244 – 2,04
Very poorly	0,20 - 0	2,04 - 0

III. Conclusions

1. The task of determining the aggregate objective function is set, with which to assess the complex effects of substances contained in coffee on the human body.

2. The construction of a summary function is demonstrated, evaluating opportunities to improve the mental stability and prevent cancer, using the function of desirability of Harrington.

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